

INTERNATIONAL GEOLOGICAL CORRELATION PROGRAMME

PROJECT 429 - ORGANICS IN MAJOR ENVIRONMENTAL ISSUES



**Proceedings of the Inaugural Meeting
Prague, September 10-12, 1998, Czech Republic**

**ORGANICS IN MAJOR
ENVIRONMENTAL ISSUES**

**Edited by
Jan Pašava**

Czech Geological Survey
Prague 1999

This international meeting was organized under the auspices of the Czech Geological Survey and the Czech IGCP National Committee and was co-sponsored by Severočeské doly a.s. and OKD a.s.

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Cover photograph: Abandoned open pit at Hromnice near Pilsen (west Bohemia), where pyritic black shales were mined in the past for the production of the Bohemian sulfuric acid.

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IGCP PROJECT 429 "ORGANICS IN MAJOR ENVIRONMENTAL ISSUES" (1998-2002): RECENT ACTIVITIES AND FUTURE PLANS

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Introduction

IGCP Project #429 "Organics in Major Environmental Issues" (1998-2002) was approved by UNESCO in February 1998. In the period from March, 1998 to October 15, 1998 which was the first year of the Project around 70 scientists from 31 countries participated in the Project activities.

The configuration of the Project is as follows:

National Working Group

Suggested Representative

Argentina	M. Brodtkorb
Australia	B. Lottermoser
Austria	H. Lobitzer
Bulgaria	T. Todorov
Brazil	Laecio Cunha de Souza
Canada	J.F. Barker
China	Fan Delian
Czech Republic	B. Křibek
Estonia	E. Puura
Finland	K. Loukola-Ruskeeniemi
France	M. Leblanc
Germany	K. Bosecker
Hungary	M. Polgári
Israel	Y. Chen
Italy	P. Lattanzi
Japan	S. Nakashima
Korea	H.T. Chon
Macedonia	T. Serafimovski
Mongolia	B. Tumenbayar
Nigeria	S. Akande
Philippines	E.C. Santiago
Poland	W. Mayer
Romania	C. Dinulescu
Russia	A. Kontorovich
Slovakia	I. Rojkovič
Slovenia	T. Dimkovski
South Africa	K. Walemba
Spain	I. Suarez-Ruiz
Switzerland	J. Spangenberg
United Kingdom	J. Parnell
United States	T. Giordano

1. Achievements of the Project this year

1998 was the first year of the IGCP Project #429, characterized by the organization of its structure and by delineation of its scope and aims. National Working Groups or Correspondents have been established in 31 countries.

Newsletter #1, including full description of the Project #429 and the proposed agenda for the Inaugural Meeting, was distributed to all participants shortly after approval of the Project.

The activity of virtually all the newly formed National Groups was concentrated on the formulation of the goals which were to be discussed at the Inaugural Meeting of the Project.

The Inaugural Meeting of the IGCP #429 was held in Prague, Czech Republic between September 10-12, 1998. The two day meeting was followed by a one day field trip. Forty one participants from 20 countries took part in this event with the aim to present and discuss the proposed Project management structure, work plan, schedule of annual international meetings, creation of working groups as well as publication policy. At the very beginning, the following basic information about IGCP and its rules were presented by Jan Pašava:

Purpose and objectives of the IGCP

- co-operative enterprise of the IUGS and UNESCO
- idea to create IGCP was suggested at a joint IUGS-UNESCO Meeting in October 1967 in Prague with the final approval in 1972
- the first meeting of IGCP Board took part in May 1973 in Paris

Purpose:

- to encourage and facilitate international co-operation in research on geological problems and thereby to promote the wise use of the Earth as a human habitat, as a source of natural resources and to reduce the effects of natural disasters

Objectives:

- increasing our understanding of the factors controlling the global environment in order that living conditions may be improved
- developing more effective ways in finding and assessing natural resources
- increasing our understanding of geological processes and developing new geological concepts in order to meet future human needs
- improving research capacities, methods and techniques of research, through international collaboration of scientists from developed and developing nations
- promoting transdisciplinary co-operation, especially within the framework of UNESCO, on joint programmes of global importance

IGCP general policies

- new projects are approved by IGCP Scientific Board (16 members) for a period of not more than 5 years
- project leader must submit to UNESCO an annual report by 15 October each year which is reviewed by IGCP Scientific Board (new projects reviewed after 2 years)
- it is important that project leader receives from National Representatives a summary report covering major activities (national meetings, major scientific highlights, planned workshops or field excursions for the year ahead) by September 1, each year
- level of financial support allocated annually from UNESCO and IUGS is based on the results of the reviewing process and money can be used to:
 - cover part of organizational expenses
 - facilitate participation of active scientists preferably from developing countries in plenary meetings of the project (requests directly to project leader/s)
 - NO RESEARCH AND PUBLISHING MONEY AVAILABLE FROM IGCP BUDGET
- scientists participating in a project should keep in touch with their National Representative who has to be approved by IGCP National Committee
- each publication which is a contribution to an IGCP should possibly bear IGCP logo and the IGCP project should be mentioned in acknowledgements
- one copy of each publication should be sent to project leader who should attach it to the Annual Report for UNESCO

Following the official opening of the IGCP 429 Inaugural Meeting, the proposal for the IGCP 429 Management Structure and IGCP 429 - MAB (Man and Biosphere UNESCO Programme) initiative were presented, discussed and approved by the participants:

IGCP 429 management structure

Co-Leaders: Jan PAŠAVA (IGCP) (CZECH REPUBLIC)
<pasava@cgu.cz>

Jan JENÍK (MAB) (CZECH REPUBLIC)
<jenik@natur.cuni.cz>

Scientific Secretary: Andrew Paul GIZE (UNITED KINGDOM)

<andy_gize@email.msn.com>

Regional Vice-Leaders:

Kagumbu WALEMBA (AFRICA)
<065KABUN@cosmos.wits.ac.za>

Delian FAN (ASIA)
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Bernd LOTTERMOSER (AUSTRALIA)
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Kirsti LOUKOLA-RUSKEENIEMI (EUROPE)
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Laecio CUNHA DE SOUZA (SOUTH AMERICA)
<laecio@geologia.ufrn.br>

It must be stressed that the IGCP 429 is unique in being the the first IGCP Project to be internationally co-ordinated by a geoscientist (Dr. Jan Pašava - experienced leader of several IGCP Projects from the Czech Geological Survey in Prague) and a biologist (Dr. Jan Jeník - MAB chairperson from the Department of Botany, Faculty of Science, Charles University in Prague). The primary objective of this collaborative venture is to integrate varied groups of geoscientists and biologists in order to bridge a gap between two major UNESCO Programmes - IGCP and MAB, and thus serve our society more effectively. After introduction of Man and Biosphere Programme, Prof. Jenik has strongly encouraged all the participants to get in touch with local MAB representatives in order to inform them about IGCP 429 activities with the aim to initiate joint studies.

The participants have agreed that the IGCP 429 will become together with the Czech Geological Survey and UNESCO/Paris one of the co-organizers of the GEOCHIM postgraduate course in Exploration and Environmental Geochemistry. Adding a "training component" and encouraging the involvement of more people especially from developing countries will be another very important aspect of IGCP 429 activities. This course will be held in Prague and Dolní Rožínka (Czech Republic) from September 7-20, 1999 and more information is available at GEOCHIM, Czech Geological Survey, Geologická 6, 150 00 Praha 5 - Barrandov, Czech Republic, phone : +420-2-5817390, fax: +420-2-5818748, e-mail <kribek@cgu.cz> or <pasava@cgu.cz>.

Jan Pašava has emphasized major goals of the IGCP 429:

IGCP 429 major goals

This project is intended as a means of bridging gaps especially between IGCP and MAB activities involving geoscientists, biologists and health specialists, to encourage cross-fertilisation of skills and ideas, and to co-ordinate research efforts in order to be of great value to society as possible.

This project should help society through studies of organic-metal interactions and the weathering process of fossil organic matter and associated sulphides in developing more sophisticated and effective remediation policies, and treating acid mine drainage from active and former mining areas, thus contributing to the prediction, minimization, and treatment of the negative environmental impacts of mining activities on our planet.

This project should provide society with very useful analogues to assess the performance of radionuclide containment at man-made radioactive waste repository sites, thus making repository processes more safe.

This project should help society, through compilation of environmental models, to develop safer exploitation of industrial, widely occurring, black shale hosted mineral deposits.

This project should help society to identify organic atmospheric factors ranging from environmental to health deterioration, thus to help to become aware of, and minimize, negative impacts of human living.

This project should help society to distinguish various sources of traceable organic pollutants in aquifers, thus to contribute to the evaluation of water pollution risk.

After acceptance of the IGCP 429 structure and introduction to the IGCP 429 main goals, six keynote lectures (20 min. each) addressed major topics within the IGCP 429. Twenty three talks were presented by scientists from 20 countries during the two full day sessions, which were well attended by 41 participants. The concluding discussions resulted in the constitution of the following eight thematic working groups:

Topical working groups

WG1: Organic matter - metals interaction

(A.P. Gize, UK - e-mail: <andy_gize@email.msn.com>

WG 2: Microbial leaching in environmental clean up

(K. Bosecker, Germany - e-mail: <k.bosecker@bgr.de>)

WG 3: Weathering of organic matter

(B. Kříbek, Czech Republic- e-mail: <kribek@cgu.cz>)

WG 4: Acid mine drainage

(E. Puura, Estonia - e-mail: <epuura@math.ut.ee> or <erx@ket.kth.se>)

WG 5: Environmental models of black shale hosted mineral deposits

(W. Mayer, Poland - e-mail: <wmayer@geol.agh.edu.pl>)

WG 6: Organic atmospheric particulates

(K. Hall, U.K. - e-mail: <Keith_Hall_GC2@compuserve.com>)

WG 7: Organic matter in nuclear waste issues
(D. Mossman, Canada - e-mail: <drossman@mailserv.mta.ca>)

WG 8: Organics in aquifers and water systems
(L. de Souza <laecio@geologia.ufrn.br> and R. Melo, Brazil, J. Spangenberg, Switzerland
<Jorge.Spangenberg@imp.unil.ch>)

Finally, a schedule of annual major international meetings was arranged for the duration of the IGCP 429:

Annual international meetings

- 1998 - Inaugural Meeting, Prague, Czech Republic (September 10-13)
(done)
- 1999 - Annual International Meeting (session 2 “Organics in the formation and remediation of mineral deposits”, within the 5th SGA-IAGOD Meeting), London, U.K (August 25-28) - confirmed
more info at [http:// www.immr.tu-clausthal.de/sga.html](http://www.immr.tu-clausthal.de/sga.html)
- 2000 - Annual International Meeting (within the 31st IGC),
Symposium C-7 “Organics in Major Environmental Issues”
Rio de Janeiro, Brazil (August 6-17)
- 2001 - Annual International Meeting (within the 6th SGA Meeting),
possibly in Krakow, Poland ?
- 2002 - Final Meeting in a country with the most advanced research
(most likely at the GAC/MAC Meeting in Canada or GSA Meeting in USA)

The meeting was followed by a one day field trip to the North Bohemian Coal Basin, co-organized by the North Bohemian Coal Mining Joint Stock Company. It has been documented in several case studies that lignite mining and waste heap remediation have to address problems such as the generation of acid mine drainage, and various agrochemical properties resulting from newly formed organic substrates. Such issues will be evaluated during the IGCP 429.

It has been agreed that an IGCP 429 WEB SITE will be set up by A.P. Gize (UK) <andy_gize@email.msn.com> who will announce its precise address to all the participants.

The participants of the Inaugural Meeting have agreed to e/mail about 1 page abstract of their talks presented at the meeting to Jan Pašava <pasava@cgu.cz> by September 30, 1998. They will be printed in the Proceedings of the IGCP 429 Inaugural Meeting and distributed to the participants.

Newsletter #2, describing the Inaugural Meeting of the IGCP 429 was distribute to all the participants shortly after the meeting.

2. List of meetings with approximate attendance and number of countries

IGCP 429 Inaugural Meeting

(September 10-12, 1998, Prague, Czech Republic)

41 scientists from 20 countries

3. Number of publications

Proceedings of the Inaugural Meeting will be published at the end of 1998 in the printing house of the Czech Geological Survey (Prague). Excursion guide to the Inaugural Meeting of the IGCP 429 was prepared by J. Godany and B. Kříbek from the Czech Geological Survey.

4. List of countries involved in the project (* countries active in 98)

Argentina, Australia, *Austria *Bulgaria, *Brazil *Canada, *China, *Czech Republic, *Estonia, *Finland, *France, *Germany, *Hungary, *Israel, *Italy, *Japan, *Korea, *Macedonia, *Mongolia, *Nigeria, *Philippines, *Poland, *Republic of South Africa, *Romania, *Russia, *Slovakia, Slovenia, *Spain, *Switzerland, *UK, *USA,

5. Activities involving other projects, IUGS or major participation of scientists from developing countries

It must be stressed that the IGCP 429 is unique in being the the first IGCP Project to be internationally co-ordinated by a geoscientist (Dr. Jan Pašava - experienced leader of several IGCP Projects from the Czech Geological Survey in Prague) and a biologist (Dr. Jan Jeník - MAB chairperson from the Department of Botany, Faculty of Science, Charles University in Prague). The primary objective of this collaborative venture is to integrate varied groups of geoscientists and biologists in order to bridge a gap between two major UNESCO Programmes - IGCP and MAB, and thus serve our society more effectively.

The Project will become together with the Czech Geological Survey and UNESCO/Paris one of co-organizers of the GEOCHIM postgraduate course in Exploration and Environmental Geochemistry. Involvement of more people especially from developing countries will be another very important aspect of IGCP 429 activities.

6. Proposed activities of the project for the year ahead

General goals:

Based on the approved IGCP #429 work plan the following activities were proposed for 1999:

- Development of new and continuation of ongoing transdisciplinary research projects covering the eight major topics of the Project with possible involvement of MAB specialists on both national and international levels
- Active participation in GEOCHIM postgraduate training course on the exploration and environmental geochemistry
- Presentation of scientific results on both national and international levels
- Publication of new results in local and internationally recognized periodics

- Editing Newsletters
- Updating Project web site

Specific Meetings and Field Trips:

1. Annual International Meeting

- session 2 - "***Organics in the formation and remediation of mineral deposits***",
- co-convenors: A. Gize, J. Pašava and A. Fleet
- organized within a joint SGA-IAGOD Meeting, London, U.K (August 25-28, 1999)
- more info at [http:// www.immr.tu-clausthal.de/sga.html](http://www.immr.tu-clausthal.de/sga.html)

2. GEOCHIM - training course in exploration and environmental geochemistry

- co-organized with the Czech Geological Survey and UNESCO,
- Prague and Dolní Rožínka, September 7-20, 1999
- more information at <pasava@cgu.cz> or <kribek@cgu.cz>

Proposed Major Publications:

Chapter in a hard cover proceedings of the SGA-IAGOD International Meeting in London (A.A.Balkema Publisher).

7. Other relevant information

It has been recommended at the Inaugural Meeting in Prague, that the IGCP Secretariat in Paris should consider informing MAB Secretariat in Paris about newly initiated activities and ask for any help in distributing this information through individual MAB National Committees as possible.

8. Acknowledgements

The Project leadership wishes to express best thanks to the Czech Geological Survey in Prague, Severočeské doly a.s. and OKD a.s. for their significant sponsorship of the Inaugural Meeting.

The following text summarizes abstracts of presentations in alphabetical order, which were given at the Inaugural Meeting of the IGCP 429 “Organics in Major Environmental Issues” in Prague (September 10-12, 1998), Czech Republic.

ENVIRONMENTAL CONTAMINATION OF TOXIC HEAVY METALS IN THE VICINITY OF SOME HISTORICAL GOLD AND BASE METAL MINES IN THE JESENÍKY MTS. (CZECH REPUBLIC)

Jaroslav Aichler and Vratislav Pecina

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The Jeseníky Mts. represent the Variscan segment of the NE Bohemian Massif with mineralization bound to the Devonian volcano-sedimentary sequences polyphasely thrust, folded and metamorphosed. Gold and base metal ore deposits were mined here intensively in the medieval and subrecent years.

The study will focus on soils, plants and stream sediments in the ancient gold-bearing Andělská Hora ore district in which the mining and processing activities have caused the

contamination by heavy metals. The probable exploitation of gold started here in prehistoric time (Aichler et al. 1988) and continued until end of 19th century (Novák 1977).

The vein-veinlet low sulphide Au-quartz mineralization of this district is hosted by carbonaceous slates, altered tuffs and dolerites of the Devonian Vrbno Group. The polyphasely folded, thrust and metamorphosed Fe-rich carbonaceous chlorite-muscovite slates enriched in Fe-sulphides and Fe-Mg carbonates appear to have been the favourable screen for reducing of the ascending metamorphic – hydrothermal fluids. Massive influx of the H₂O-CO₂ fluids derived from the devolatilisation of the metamorphic pile caused extensive beresit-listvaenite metasomatic alterations of the rocks. Goldbearing carbonate-quartz veins and veinlets are located in different planes of cleavage and joints connected with superposed fold deformation (D1-D4) and polyphase metamorphism of greenschist facies (M1-M4). Gold precipitation within the pyritic and carbonaceous slates may be ascribed to changing pT-conditions, decreasing of pH and H₂S-activity at low f_{O₂} (Aichler 1992).

There exists a lot of geochemical data originating from the regional prospecting (geochemistry of stream sediments, surficial waters) and geochemical research campaigns (soil geochemistry, waters) in the district and its vicinity from the sixties to the eighties which could be used and assessed from the point of view of the contamination by mining activities.

In the framework of the IGCP Project 429 we also plan to collect a smaller set of samples of soils, stream sediments and plants in the area below the medieval processing plant in the centre of the Andělská Hora ore district where the most intensive contamination by As, Ag, Pb, Zn and other elements has been encountered during the geochemical prospecting. The results of the correlation of data and the extent of contamination will be used in the assessment of the potential risk for the local inhabitants.

MICROBIAL LEACHING IN REMEDIATION PROCESSES

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As a consequence of technological and industrial development many industrial sites are contaminated with heavy metals and/or organic compounds. The main problem of these anthropogenic wastes is that they are toxic for organisms of any kind and, particularly, for human beings. Therefore it is important to remove or minimize these metal and organic contaminants in order to minimize the health hazard associated with the uptake of food and air and to prevent contaminants being dissolved and distributed by surface and ground water.

Organic contaminants may be degraded biologically, and CO₂ and water are the final products. Other than with organic compounds heavy metals cannot be decomposed, neither biologically, chemically nor physically. Metals may be solubilized, they may be changed in valence or in chelating state, they may be immobilized, but they are still metals. At low

concentrations many metals are essential parts of metabolic processes but at high concentrations they are toxic and a careful clean up is necessary to save our environment.

Microbial leaching is a simple and effective technology for extracting valuable metals from low-grade ores and mineral concentrates. This is done by microbial acid production, e.g. formation of sulphuric acid by oxidation of sulphur and reduced sulphur compounds, by oxidation of Fe^{2+} to Fe^{3+} which then functions as a chemical oxidant, by the excretion of organic acids, and by changes in oxidation states. Besides the industrial application for raw materials supply microbial leaching has some potential for remediation of mining sites, treatment of mineral industrial waste products, detoxification of sewage sludge and for remediation of soils and sediments contaminated with heavy metals.

There is no routine treatment for toxic metals dispersed in solid materials and autotrophic and heterotrophic leaching processes may be considered for environmental clean up. The problems of metal ion bioremediation are very different from those of organic bioremediation, but investments in intensive interdisciplinary collaborations between basic and applied scientists in this economically important area can be expected to yield dramatic returns in the near future.

The ideal situation exists when the bioremediation system is designed to maximize both the extent and rate of degradation of waste material and minimize the level of toxic substances during the operation.

ASSESSMENT OF NITRATE CONTAMINATION IN THE BARRIERAS AQUIFER AND APPLICATION OF ISOTOPIC GEOCHEMISTRY ON QUALITY CONTROL OF DRINKING WATER IN METROPOLITAN NATAL, RIO GRANDE DO NORTE STATE (NORTHEAST BRAZIL)

Laécio Cunha de Souza*, **Marcelo Augusto de Queiroz****, **Johannes Hunziker*****
and **Jorge Enrique Spangenberg*****

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BFSH-2, e-mails: johannes.hunziker@imp.unil.ch or Jorge.Spangenberg@imp.unil.ch*

Introduction: The studied region is located on the coast line of northeast of Brazil where the city of Natal and the neighboring cities of Extremoz, São Gonçalo do Amarante, Macaíba and Parnamirim are located, encompassing about 500 km². The local basin belongs to the system of inshore basins of northeast of Brazil. It is composed of sedimentary units evolving from

Craceous to Quaternary. The Barreiras Group, constituent of the superior unit, is composed of sandy - clay sediments of tertiary - quaternary age. This Group is beneath recent sediments of sand dunes, capped by an alluvial sequence.

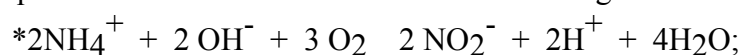
The water provision system is expressed by wells, some fountains, some superficial water courses and some ponds. The analyses of variations of the hydraulic loads in the wells and also of the lithostructural character of the sedimentary layers suggest that the sequences of dunes and the Barreiras sediments form a unique and complex hydraulic system. Generally, it presents a behavior of a free aquifer.

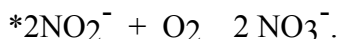
General aspects of system Dunes/Barreiras aquifer: The hydrochemical survey of the underground waters of the metropolitan Natal indicates that the superficial and shallow (< 30 m) waters are in general calcic bicarbonate. The deeper waters are rich in chlorine and sodium. They are also in general acidic (pH= 5.5), of low salinity with and electric conductivity of the order of 200 S/cm.

According to the Company of the Waters and Sewers of Rio Grande do Norte State (CAERN), a volume of the order of $80 \times 10^6 \text{ m}^3/\text{year}$ is pumped from underground and superficial (ponds) reservoirs. The volume of underground exploited water by the tubular wells is of the order of $52 \times 10^6 \text{ m}^3/\text{year}$, which represents 73% of the whole of the water used by the city. The remaining water (27%) comes from ponds (Jiqui and Extremoz). The metropolitan population is around 800,000 inhabitants and the demand reaches $72 \times 10^6 \text{ m}^3/\text{year}$. The exploited reserves (considered equivalent to the out-flow of water by the natural flux) are of the order of $116 \times 10^6 \text{ m}^3/\text{year}$. Taking into account the exploited volume by wells of the order of $68 \times 10^6 \text{ m}^3/\text{year}$, it could be conclude that in the present conditions there is an average availability of water of $48 \times 10^6 \text{ m}^3/\text{year}$. In this case, the permanent reserves are invariable.

Aspects of drinking water deterioration: The underground waters of the Metropolitan Natal is vulnerable to deterioration processes due to anthropogenic activities, to the utilization of septic pits system and to irregular and disorganized soil occupation. The nitrate is mostly original from biodegradation of human excrement. In addition to the septic pits and the disorganized urbanization, some other activities, such as industry, sanitary landfill, gas stations, car repair garages, hospitals, brewery and cemeteries, offer important risks of contamination to the underground water system. It is well known that several leather, food, textile, drugs and brewery industrial activities contribute with organic matter and the organo synthetic components as contaminants. Total residue was quantified as $3.3 \times 10^6 \text{ m}^3$ the large contribution being from domestic origin and, in a lesser extent, from hospitals. Only 20% of these materials are recycled. The garbage processing plant is located on the dunes at the main refill zone of the aquifer system. The potential sources of deterioration of the underground waters are very little studied and their effects on the aquifer are also unknown. The infrastructure for collection of sewage and domestic and industrial waters covers only 20 % of the city of Natal.

The contamination by deterioration of the organic matter (Nitrates): Since 1986, CAERN has tried to quantify the contents of nitrates in the waters. So far, several wells stopped production due to contamination ($\text{NO}_3^- > 100 \text{ mg/l}$). The procedure of dilution is adopted by this company in order to lower the content of nitrates of several well that can not stop production. The waters used for this dilution comes from some ponds and wells located in the non contaminated zones. Generally, it exists an interrelationship between the demography and the content of nitrates in the underground waters. Probably the oxidation of ammonia from the septic pits is the principal responsible for the raised concentration of nitrates in the underground waters (nitrification*). The vulnerability for contamination of the Dunes/ Barreiras aquifer in Natal was assessed as moderate to high.





Application of stable isotopes to the environment: Measurements of Oxygen and Nitrogen isotopes for the different components of the nitrogen cycle offer the unique possibility to characterize the sources of nitrogen (for example: fertilizers, human garbages, NO_x from the consumption of the fossils fuels, etc.), its transport and transformation. The first isotopic data (¹⁵N) from the underground waters of the Natal region (six analyses) were measured by the Laboratory of Isotope Geochemistry of Lausanne, Switzerland . The values of ¹⁵N are between 7.8 and 13.8. The value of 13.8 indicates a contamination by human excrements (septic pits). The lower values could be explained by dilution of the nitrates.

Finally, our future investigations will be particularly important since it will give guidelines to political decisions in terms of investments in sanitary infrastructures to improve the public health, in order to protect the quality of drinking waters used by the population of the Metropolitan Natal.

COMPOSITIONAL CHARACTER OF DACHANG SN-POLYMETALLIC ORES AND ITS INFLUENCE ON ENVIRONMENT

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In Dachang ore field of Guangxi Zhuang Autonomous Region, there are many Sn-polymetallic deposits with different scales. The total reserves in this field are more than 170 x 10⁶ tons metals, including 705 x 10⁴ tons of metals (Sn, Zn, Pb, Sb, Cu, W etc) and 1031 x 10⁴ tons non-metals (S and As). The Tongkeng-Changpo and Longtoushan Sn-polymetallic deposits are super-large in scale and account for around 80 percent of the total reserves in Dachang ore field.

The Tongkeng-Changpo deposit is located in the western part of the Dachang ore field. The major part of the Upper Devonian strata has a total thickness around 200m and can be divided into:(1) Liujiang Fm. (Frasian Epoch,40m thick) is composed mainly of black chert, in which are located the largest ore body No.92 in stratified and strata-like form, conformable with black chert layers.(2) The Wuzhishan Fm.(Famenian Epoch,102m thick) is composed mainly of banded, laminated and lenticular limestone (marl) with chert and siliceous shale. The large ore body No.91 is located in forms of elongate strata-like lenticles within black chert. The ores are massive, banded, laminated and disseminated. The major

minerals are cassiterite, pyrite, pyrrhotite, sphalerite, arsenopyrite, jamesonite, quartz, tourmaline, adularia, calcite etc. The host rock is black chert, the country rocks are shale - marl.

The Longtoushan reef is a long time developed reef (from Upper Emsian to Givetian) with autochthonous biolithite and allochthonous bioclastic limestone rock association. The reef-building organisms are Stromatopora, Tanulata with various ecologic types, the reeplilic organisms include Echinodermata, Brachiopoda and Bivalves. Ore bodies are strata-like and vein type, the latter is represented by the largest ore body No.100 with 900m long, 60-230m wide and mean thickness of 12.61m. Ore minerals are pyrite, arsenopyrite, galena, sphalerite, pyrrhotite, jamesonite, cassiterite etc. Gangue minerals are quartz, adularia, calcite and siderite etc.

The ore bodies of Tongkeng-Changpo and Longtoushan are located in the black shale series of Middle-Late Devonian strata. The host rocks are mainly of chert and carbonate rocks with high content of organic matter (mean around 1-1.5%). The ore bodies are stratified, strata-like, disseminated and in vein type. The ores are characterized by multi-element association (including Sn, Sb, Pb, Zn, Au, Ag, Cu, Hg, W, Se, Tl, Re, In, Cd, Ga etc) and complex mineral assemblages, including sulfides, sulfosalts, oxides etc. Therefore, the mining and processing processes represent a process of oxidation of organic matter, sulfides and arsenides of Fe, Cu, Pb, Sb, Sn etc. Especially under the hot and humid climate in South China, the mining and processing process of the huge amount of sulfides and arsenides constitute the pollution of the environment in the ore field.

ORGANICS AND METALS IN ENVIRONMENTAL ISSUES

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The environmental impact of metals from natural and anthropogenic sources depends in part upon their speciation. Current research is focussed on the alkylmetals (Pb, Sn, Ge, As, Hg) in northwest England. Concern on such compounds stems from their very high vapour pressures and solubility in lipids (e.g., cell membranes). In the alkylmetals, carbon is more electronegative than the metal, in contrast to many anthropogenic and biochemical organic compounds. As a first order approximation, the electronegativity difference between lead and carbon is comparable to that between carbon and chlorine.

The alkylmetals have been synthesised for nearly 150 years. The first organolead compound was synthesised by Löwig in 1853. By 1965, 1200 organolead compounds were known. The first organotin compound was synthesised by Frankland (1849), by heating tin with ethyl iodide in a sealed tube. Their industrial uses, however, commenced relatively recently. Tetraethyllead is still used in some countries, including the United Kingdom, as an anti-knocking component in petrol, both automotive and aviation. Current research is showing anomalies in river waters resulting from road bridges.

Organotins have found industrial applications even more recently than lead. In spite of the advantages of the clear plastic, PVC, in terms of moulding and cost, it shares in common with other organic polymers, susceptibility to elevated temperatures and UV light. PVC

stabilisation was a major use of organotins in the mid-1980s, accounting for 20,000 tonnes annually. Bis (tributyltin) was introduced as a wood preservative in 1959, and applied as a 3% solution in kerosene, together with insecticides, as a fungicide. Degradation of tributyltin to the less biologically active dibutyltin has been reported.

Organotin compounds are present in the waters and sediments of NW England estuaries, reflecting their initially widespread use in antifouling paints. Marine fouling increases the surface roughness of a ships' hull, and therefore increases its' friction to movement in water. This results in loss of speed, increased fuel expenditure, and increased time in dry dock for scraping. Fouling has been of concern for centuries. Athenius, 2000 BC, reported that "The ships of Archimedes were fastened everywhere with copper bolts and the entire bottom was sheathed with lead". In 300 BC, arsenic compounds and sulphur were combined with wax and tar to coat ships' hulls. In 1860, a soap based on copper sulphate was used as the first anitfouling paint. Although organotins were highly successful antifouling compounds, current environmental concern lies in their "imposex" properties.

Our current analytical methodology is based on Moens, which involves ethylation in the water sample to form the volatile compounds. The volatiles are then adsorbed on to coated glass capillary columns (solid phase microextraction, SPME), prior to desorbtion in a heated gas chromatograph injection port for ICP-MS analysis.

STUDY OF ORGANIC ATMOSPHERIC PARTICLES

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Micro-Scaled Sealed Vessel pyrolysis (MSSV) is a soft pyrolysis technique developed for use in organic geochemistry to study oils and source rocks. It differs from conventional pyrolysis techniques in that oxidative formation of any secondary artefacts can be minimised [1]. It has since been applied to other fields of analytical chemistry [2] including the investigation of atmospheric dust [3].

Understanding of the chemical and physical behaviour of atmospheric particles is very much in its infancy. Interest has grown from reports such as the Committee on the Medical Effects of Air Pollutants (COMEAP) report [4] which attributes 8,100 mortalities to PM₁₀ with a further 10,500 hospital admissions for respiratory problems in urban areas of the United Kingdom alone. This effect is expressed as a function of the aerodynamic particulate size, however the cause for these increases is not fully understood but some chemical effect may be partly responsible. Understandably then it is the respirable fraction of atmospheric particulates (PM₁₀) that has been of most concern.

The carbonaceous fraction of PM₁₀ ranges from 20 to 70% of the total deposit and can be subdivided further into carbonate (\approx 5%), elemental carbon (\approx 15-35%) and organic compounds (\approx 60-80%) which means that up to 50% of the total PM₁₀ mass can be organic in nature. A substantial amount of analytical investigation of the inorganic components using various techniques has led to a good understanding of this fraction [5], however, the organic

fraction of PM₁₀ particulate is poorly characterised [6]. To date the most common analysis carried out on PM₁₀ has been solvent extraction of sampled filters but this only provides restricted information as volatile compounds tend to be lost. Therefore, emphasis has been placed on a number of target compounds such as the Polynuclear Aromatic Hydrocarbons (PAH's) and Nitro-PAH's [7,8]. Limited data have been produced for the volatile components [9] and little is known about the majority of semi-volatile compounds.

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GEOAEROSOLS, THEIR ORIGIN, TRANSPORT AND PARADOXICAL BEHAVIOR: A CHALLENGE TO ORGANOMETALLICS

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Association of toxic heavy metals with geologically derived organic material (organometallics) has been well established. Recently, an International Working Group on Medical Geology (<http://hem1.passagen.se/dse2725/bookon.htm>) has convened to investigate the link between geology and morbidity and mortality. The formation and transport of toxic

metallic and organic-metallic substances in nature is crucial for understanding any health impact they might exert.

The key point of this paper is to report that we have observed a previously overlooked source and mechanism for the transport of these toxic heavy metals into the atmosphere, which is completely different from the usually assumed transport mechanism of volatile methylated metallics.

This new mechanism is aerosol transport from natural geologic sources, distinguished from geogas because geoaerosols have a greater affinity for adhesion to solid surfaces, such as the lung. In fact, inhaled heavy metals have been implicated in causing runaway immune system activity threatening individuals whose respiratory system is already compromised with asthma or other chronic lung diseases (Science News, v. 153, p. 68).

We observed that deep in isolated and sealed off cave or mine atmospheres there are aerosols of 3 to 200 nm size present at concentrations ranging from few tens to several thousands per cm³. We used standard aerosol equipment (TSI 3025A condensation nuclei counter with a diffusion battery, TSI 3040), together with radioactive counting of Pb-210 and Po-210 to determine the size, concentration and transport of these aerosols, noting that Pb and Po can be used as surrogates of other heavy metals in these aerosols. Simultaneous measurements of radioactive aerosols inside and outside the mine and cave showed that the inside aerosols are inorganic and as radioactive, as one would expect if they originated in the rock and soil. Outside aerosols were usually at concentrations an order of magnitude higher than that from underground, were mostly organic in derivation, and had radioactivity hundreds of times lower than the underground aerosols, again as would be expected from outside aerosols.

The concentration of outside aerosols varied in relation to environmental and anthropogenic influences. For example, a rain would decrease the concentration, and sunlight, causing formation of small aerosols by UV light from plants released terpenes, and the passing of a car, would increase the concentration.

Underground, there were episodic increases of aerosols up to 15 times the baseline concentration. Eventually, the aerosols from these underground bursts will enter the atmosphere, even though they are usually hard to detect due to prevalence of other aerosols. In geochemical exploration, the aerosols have been called geoaerosols and have been noted to be more numerous over very porous or faulted ground, and have been suggested and successfully applied as an exploration technique for finding heavy-metal deposits.

Although the mechanism of transport and release is still under study, based on our observations, we conclude that geoaerosols represent an important source and mechanism for the transport of trace and toxic metals and that it significantly contributes to the atmospheric burden of metallic compounds.

DISPERSION AND ENRICHMENT OF POTENTIALLY TOXIC ELEMENTS IN AREAS UNDERLAIN BY BLACK SHALES AND SLATES OF THE OKCHON ZONE IN KOREA

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Potentially toxic elements are highly enriched in Okchon black shale in Korea. The Chung-Joo, Duk-Pyung, Geum-Kwan, I-Won, Bo-Eun and Chu-Bu areas are underlain by these black

shales and slates of the Guryongsan Formation or the Changri Formation, which are parts of the Okchon Group in the central part of southern Korean Peninsula. Environmental geochemical surveys were undertaken in the above study areas in the Okchon Zone. After appropriate preparation, rock and soil samples were analysed for multi-elements by INAA, ICP-AES and EPMA, and plant samples by AAS. The objectives of this study are 1) to investigate the enrichment levels and dispersion patterns of toxic elements within the rock-soil-plant system in areas underlain by black shales and slates, 2) to evaluate the uptake ratios of trace elements from soils into crop plants, 3) to assess the chemical speciations of trace elements in soils, and 4) to identify uranium-bearing minerals in black shales and residual soils derived from black shales.

In particular, As, Ba, Cd, Mo, V, U and Zn are highly enriched in Okchon black shales, and their mean concentrations are significantly higher than those in black slates. The highest mean concentrations of 42.0 µg/g As, 2100 µg/g Ba, 10.9 µg/g Cd, 213 µg/g Mo, 83 µg/g U, 938 µg/g V and 394 µg/g Zn are found in black shales from the Duk-Pyung area. Mean concentrations of As, Mo and U in soils derived from black shales occurring in the Duk-Pyung area (30 µg/g As, 24 µg/g Mo and 50 µg/g U) and Chu-Bu area (39 µg/g As, 15 µg/g Mo and 27 µg/g U) are higher than the permissible levels. Enrichment index values of the six study areas decrease in the order of Duk-Pyung > Chu-Bu > Bo-Eun > Chung-Joo > Geum-Kwan = I-Won areas. Relationships between element concentrations in crop plants and soils are significantly correlated. The concentration of Cd in plant species decreases in the order of lettuce > chinese cabbage > red pepper > soybean = sesame > rice stalk > corn > rice grain. The biological absorption coefficients (BAC) in plants are in the order of Cd > Zn = Cu > Pb, which suggests that Cd is more bioavailable to plants than Cu, Pb and Zn. From the result of sequential extraction analysis of soils, relatively high proportions of Cu, Pb and Zn are present as residual fractions, whereas that of Cd as non-residual fractions. Cadmium occurs predominantly as exchangeable or water/acid soluble phase in soils, and can be easily released into the environment and affect plant growth. This finding is concordant with the result that the uptake ratio of Cd in plants is the highest. Uranium-bearing minerals such as uraninite, uranocircite, uranothorite and brannerite are identified in black shales whereas francevillite is found in soils derived from black shales. Uranium-bearing minerals are closely associated with sulfide minerals such as pyrite, pyrrhotite, sphalerite and molybdenite.

The subjects for further studies in areas underlain by black shales and slates are:

- 1) to investigate the geochemical characteristics of drainage samples (sediments and natural waters),
- 2) to study the chemical speciations of trace elements in sediments,
- 3) to examine the behaviour and species of dissolved constituents in groundwater,
- 4) to investigate the mineralogical characteristics of sediments by XRD, DTA, TGA and EPMA,
- 5) to produce the quantitative modelling of water-rock interaction by mass balance calculation, and
- 6) to assess the potential environmental impacts in the area underlain by black shales and slates, in particular, on human health and disease.

UNESCO'S MAB AND PROSPECTS OF COOPERATION WITH IGCP

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Since the General Conference in 1970, UNESCO is developing and actively organising its Man and Biosphere Programme (hereafter MAB). A set of interdisciplinary projects covered by this intergovernmental initiative has been aimed at conservation of biological diversity and rational utilisation of life-supporting systems. Current trends in population growth and increasing demands for land, mineral resources and energy threaten human welfare and sustainable development at local, regional and global scales. Rational solution of related issues requires enhanced co-operation between natural and socio-economic sciences, and humanities as well. The MAB/UNESCO was a major step to overcome the isolation of individual experts in various fields of science and improve the information flow across national and disciplinary boundaries in the issues of environment and human welfare.

Currently, there are 136 sovereign National Committees which keep in touch with the MAB International Co-ordination Council (ICC), a body consisting of thirty representatives elected for three years from the entire electorate. Under the active support of the MAB Secretariat in Paris the MAB programme keeps supporting mobility of participating scientists, organising conferences, exchanging fundamental data and publishing reports and results of local and regional projects.

One of the major tools in the materialisation of the MAB programme are internationally recognised areas of terrestrial and coastal ecosystems which are called biosphere reserves and collectively constitute a World Network. They are nominated by national governments and meet a set of criteria required by the World Network. There are more than 350 biosphere reserves in all parts of the Earth, and most of them fulfil three basic functions which are complementary and mutually reinforcing: (1) conservation function, ensuring maintenance of biodiversity in core, buffer and transition zones, (2) development function, promoting culturally, socially and ecologically sustainable economic development, and (3) logistic function, providing support for research, education and information exchange with regard to local, regional and global problems.

The biosphere reserves are suitable areas for co-operation between MAB and IGCP, the two UNESCO's sister programmes. Particularly the Project 429 "Organics in Major Environmental Issues" is a highly welcome link. Both the terrestrial and oceanic ecosystems create numerous connections between mineral and biotic components. Mineral matter and rocks are involved in all biogeochemical processes which govern the life-supporting systems. Soil and most sediments are the actual interfaces between life and bedrocks. Mineral nutrition of plants, micro-organisms and animals is the basic metabolic process in all ecosystems. A variety of metals, nonmetals and organic components create the both chemical and physical environment of organisms which ultimately produce the life-supporting systems, but occasionally can threaten the welfare of human kind.

The newly established project can serve as a good basis for the development of joint actions between biologists and geologists. The biologists and ecologists welcome the increasing involvement of geologists in environmental matters, and particularly appreciate the association with the research teams which tackle the issues of heavy metals, organometals, humic and fulvic substances, water pollution, etc. Also joint studies of organic sediments, such as peat, fen and even human waste, could clarify the processes which operate in the ecosystems. Reclamation areas affected by mining offers numerous issues for joint research of MAB and IGCP scientists. Many biosphere reserves started long-term monitoring and observation comparing the untouched "core zone" with the human-exploited "transition zone", and tend to reconcile the human needs and environmental limits.

Sustainable management of water and mineral resources and careful protection of biotic diversity are the widely recognised priorities, but regional and local methods to fulfil them vary substantially according to the social and cultural habits. By inauguration of the IGCP

Project 429 the United Nations Educational, Scientific and Cultural Organisation obviously confirms its readiness to meet some of the most challenging issues of the current World.

CONDITIONS OF MS FORMATION IN MB AND ITS ENVIRONMENTAL SIGNIFICANCE

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Chinese loess is mainly distributed in the Northwest of China, where is in the mid-upper reach of Huanghe River. Loess-paleosol sequences were developed in the Loess Plateau and are associated with fluvial sediments of Huanghe River and changes of sea level, showing that loess-paleosol sequences maybe affected by global climatic changes, which control changes of sea level. In recent years, measurements of magnetic susceptibility of loess-paleosol sequences show that susceptibility of paleosol layer is higher than that of adjacent loess layer. Because changes of susceptibility are somewhat consistent with $\delta^{18}O$ changes of sea sediments, susceptibility can be used as proxy indicators in the studies of paleoclimates.

Why we should study the magnetomacteria (MB) in Chinese loess section ? What is the mechanism of changes in susceptibility ? Preceding works were focused on studies of inorganic matter, such as corrosion of $CaCO_3$, gathering of iron-bearing material caused by weathering and in situ origin new magnetic material, causing increase of the magnetic material concentration in paleosol. But it is not successful to explain. Considering that organism is most sensitive to climatic change, we started to study the distribution characteristics of organic matter in loess-paleosol sequences. Large amount of measurements of organic matter show that TOC content in paleosol is higher than that of adjacent loess, better correlated with susceptibility. Magnetotactic bacteria (MB) is a kind of bacteria which bear magnetosomes (MS) in their cells. First discovered by Blakemore in American pond, now MB has also been found in deep-sea sediments, limnetic sediments and grass soil. MS is composed of magnetite and other magnetic minerals. MB and MS maybe influence the distribution of susceptibility in loess section.

Characteristics of MB and MS in Chinese loess section

In Chinese loess section we have also found MB and MS, with relatively more MB and MS exist in paleosol. Conditions of culture of MB show that microaerobic (contain oxygen 3-10%) environment, organic iron (Ferric Malate and Ferric Quinate) rather than inorganic iron ($FeCl_3$ and $FeSO_4$) and certain iron concentration (2 –4 mM Ferric Quinate) are suitable for MS growth in cells of MB.

Significance of MS formation

During paleosol formation, the earth surface suffered from intensive weathering, forming clay minerals which act as a water tight layer to form a microaerobic environment with the overlying loess layer due to coarser grain and microporosity of loess. Time from paleosol to loess is a fluctuated climate period and has an optimal condition to form MB and MS, coincided with intensively increasing susceptibility in loess section.

When MS leave from cells of MB into sediments, forming a weak magnetic field, favorable to enrichment of transition elements in the paleosol layers.

WEATHERING OF FOSSIL ORGANIC MATTER AND RECLAMATION

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Weathering of the fossil organic matter was studied in dumpsites of the brown coal mines at the Sokolov Coal Basin (Miocene), the Czech Republic. Materials deposited in dumpsites contain both algal- and humic-type organic matter. During weathering of the organic matter, Rock Eval hydrogen index (HI) decreases from 800 to 400 (algal-type) and from 400 to 200 (humic-type). The composition of pyrolysates obtained from both fresh and weathered samples differs significantly. The relative abundance of the aromatic fraction decreases significantly in comparison with the aliphatic fraction and the amount of polars gradually increases during weathering. Changes in IR spectra show a preferential increase in the number of phenyl ester groups compared with aryl-alkyl ketone and ester groups with increasing time of weathering in both types of organic matter. ¹³C NMR confirmed an increased aromaticity of the weathered algal-type organic matter ($F_{ar} = 29\%$) compared with fresh samples ($F_{ar} = 14\%$). The increase in aromaticity of the humic-type organic matter is low (1%). Substantial amount of humic substances (up to 392 mg/g TOC) is produced during the weathering of humic-type organic matter. Only small amount of humic substances (up to 2.2 mg/g TOC, mostly fulvic acids) is produced during weathering of the algal-type organic matter.

As seen from the agrochemical point of view, weathering of the fossil organic matter and the production of humic substances affects namely the sorption properties of materials discharged in spoil banks. This is particularly evident at dumped rocks which do not contain a larger portion of montmorillonite. In montmorillonite-rich materials, the sorption capacity of organic matter is masked by the sorption capacity of the inorganic phase, regardless the weathering degree of fossil organic matter. During the weathering of humic organic matter, the C/N ratio decreases from 100 (fresh rock) to 40 (highly weathered samples). In algal-type organic matter, the same ratio decreases from 40 to 20. The decrease in the C/N ratio during weathering is explained as due to (1) a preferential loss of carbon during chemical oxidation and, (2) a microbial contribution to the nitrogen budget. The amount of microorganism in fresh and weathered samples containing organic matter of both types were monitored using microbial tests. It has been found that the amount of bacteria in weathered rocks is constrained by the low pH values and high amounts of free phenol which originate through weathering of humic-type organic matter. Biodegradation of algal- and humic types of organic matter was modeled using the ASANOL microbial culture, which is utilized for the microbial decontamination of oil spills. This microbial culture, along with a nutrient solution, was mixed with pulverized rock samples and changes in the character of spectra of extractable organic matter (aliphatic fraction) were monitored. In extracts of a biodegraded samples containing algal-type organic matter, it has been found that a considerable decrease in the amount of *n*-alkanes occurs in the range $n-C_{12}$ to $n-C_{17}$ and that pristane content substantially decreases. The results indicates that at least part of algal-type fossil organic matter may be used as a carbon source for a microbial growth. Samples containing humic-type kerogen showed no changes in the character of alkane fractions after six months.

On-going research of organic carbon- rich rocks deposited in dumpsites is focused on the fate of metals during weathering, on the microbial decomposition of the algal-type organic matter and the possibility of the microbial remediation. Study of changes in carbon and

nitrogen isotopic composition during the weathering and soil formation in dumpsites are in progress.

ORGANIC MATTER IN THE UPPER SILESIA ZINC-LEAD ORE DEPOSITS

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Black amorphous organic matter (OM) contained in large amounts in the Upper Silesian zinc-lead ore deposits has been identified as dopplerite, calcium humate. Petrological and geochemical studies of new samples of the OM confirmed the previous data published by Sass-Gustkiewicz and Kwiecińska in 1994 and 1995. Two varieties of the OM: bright and dull were observed but only one main microscopical component - euglenite was noticed. This maceral has variable reflectance changing from 0.28 to 0.36 % indicating a very low degree of coalification (maturation) corresponding to the soft brown coal stage. Lack of any remnants of organic structures belonging to inertinite and liptinite groups is evident. Chemical maceration did not reveal the presence of spores or pollens from plants which could be useful for determination of the age of primary substance.

The results of elemental analyses confirm a low degree of the OM coalification. Carbon content varies from 60-65 % (daf) and hydrogen content is between 3.2 and 3.7 % (daf). H/C atomic ratio has the values below 1.0 which are typical of humic acids derived from plant of terrestrial origin.

In the Rock-Eval pyrolyses hydrogen indices are extremely low between 8-16 mg HC/gTOC and oxygen indices vary from 61 - 92 mg CO₂/gTOC. It means that this OM has very poor hydrocarbon generation potential. We can see from the correlation between HI and OI that all samples of OM fall below kerogen type III. It means that they are humic sourced. We could already suppose that a primary source of dopplerite was terrestrial organic matter deposited in aquatic settings. This matter included woody material, spores and other plant remnants which rapidly decomposed due to aerobic bacterial activity in oxygen-rich water columns and interstitial sediment waters. So, humic acids are formed by oxidation.

FTIR spectra revealed small amount of aliphatic and naphthenic structures, a prevalence of aromatic units and a variable, but significant contribution of oxygen groups.

Molecular composition of the extracted geolipids was characterized for certain group of biomarkers on the basis of their differences in fragmentation in the ion source of the mass spectrometer. In several samples, carboxylic (fatty) acid methyl esters were detected which are characteristic of land-plant epicuticular waxes, and can be assigned to terrestrial sources. Free n-alkanoic acids were found in bright samples of the OM and in Keuper kerogen isolated from overlying Triassic shales. Mass chromatograms of n- and iso-alkanes (m/z71) extracted from selected samples and from Keuper kerogen revealed variable distribution patterns. In all samples of OM and kerogen there are elevated concentration of C16 and C18 homologues, products of palmitic and stearic acids reduction. Steranes were not detected in the studied samples. The ratio of pristane to phytane (Pr/Ph) is above unity for dull samples of OM and for Keuper kerogen and is marginally lower than unity for bright OM samples.

Considerable amounts of pentacyclic triterpanes were detected in all OM samples as well as in kerogen. Their relative abundances are however different. The observed differences in pentacyclic triterpanes composition may reflect the different postdepositional history of the examined organic substances. Keuper kerogen remained in the place of deposition, being

dispersed in overlying Triassic shales, while OM accumulated in Zn-Pb ores was affected to different extent by the migration, biodegradation and aqueous solutions. Therefore in such a case, lack of quantitative correlation in relative concentration of pentacyclic triterpanes between OM and kerogen can not exclude the latter as an humic organic matter source. The methyl-naphthalene and methylphenanthrene isomer ratios appear to be virtually identical in all samples of OM and Keuper kerogen. An allochthonous origin of OM is supported by the lack of metalloporphyrins in this material. The molecules could not survive oxidative alteration and are not susceptible to migration. Thus, dopplerite is not a native OM but a product of migration.

Dopplerite was derived from humic acids which migrated in oxidizing aqueous solutions and precipitated by the reaction with calcium ions. The precipitation was contemporaneous or penecontemporaneous with sulfide deposition at the time of initial and mature karst processes. The regional distribution of dopplerite probably depends on the availability of calcium ions generated by hydrothermal karst activity. The most probable source of humic acids seems to be an organic substance disseminated in the Keuper shales.

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MIGRATION OF ELEMENTS FROM BLACK SHALES TO AQUATIC ECOSYSTEMS AND LOCAL RESIDENTS: A PILOT STUDY IN FINLAND

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Previous studies have revealed that the presence of sulfide-rich black shales in bedrock is reflected in elevated natural baseline levels of a number of potentially toxic elements in till, surface and ground water and in stream and lake sediments. According to the study of 2000 black shale samples from drill cores all over Finland, black shales especially in eastern and northern Finland contain more potentially harmful elements on average than do other rock types (Loukola-Ruskeeniemi, unpubl. data). The concentrations of nickel and many other elements are much higher in sulfide-rich black shale areas than in the adjacent granitic or quartzitic bedrock and higher than the average values in Finland. The acidification in the lakes in black shale area in the Sotkamo municipality in eastern Finland derives from a natural source, and there is evidence that at least one lake in the black shale area was especially acidic already 9000 years ago. The concentrations of Al, Ni, Cu, Zn, Cd, and Mn in some of the dug wells in the Sotkamo black shale area are also greater than the country average for dug wells (Loukola-Ruskeeniemi et al., 1998).

Biological sequestering of potentially harmful elements has been studied in the Sotkamo and Kaavi municipalities in eastern Finland. Cool water food chains accumulate contaminants

in different ways than warm water food chains. Thus, the common interest in northern latitudes is the accumulation of potentially toxic elements into aquatic animals such as crayfish and predator fish. Coolwater crayfish are long-lived species which live and move on the sediment. According to cautious estimates, the biomass of crayfish (*Astacus astacus*) may be as much as 100-300 kg/ha in small lakes and rivers in Finland. This suggests that crayfish may play a significant role in the migration of potentially toxic elements in some Finnish aquatic ecosystems. Crayfish take up mercury via respiration as well as directly by ingesting food, and the mercury becomes concentrated in various organs and tissues (Allard and Stokes, 1989). In the Kaavi study area, mercury concentrations were found to be higher in specimens of freshwater crayfish muscle tomes collected from lakes in black shale catchment area (male 0.2 µg/g and female 0.3 µg/g) than in those collected from lakes in granitic terrain (male 0.13-0.15 µg/g and female 0.17-0.21 µg/g). In the black shale areas in Sotkamo, a natural crayfish population was not found.

The research was focused on eastern Finland because there appears to be a spatial correlation between the distribution of sulfide-rich black shales and the prevalence of coronary heart disease (CDH). Although genetic factors and living habits may be significant, trace elements in drinking water and food are also implicated, since high concentrations of potentially harmful trace elements in the geological environment and low selenium intake have been found to correlate with higher incidence for CDH (Salonen et al., 1991,1995). Fish and fish products are probably the dominant source of methylmercury in food. Results of our pilot study suggest a relationship between Hg concentrations in humans and geological location of well used for drinking water. From the Sotkamo municipality, 36 people participated in the pilot study. Those who lived in black shale area and got their drinking water from a dug well, had 4.26 µg/g mercury in hair, compared with the average of 2.8 µg/g in the whole population.

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ORGANIC MATTER IN NUCLEAR WASTE ISSUE

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Almost 2 billion years ago nature concocted over a dozen nuclear fission reactors in uranium ore at Oklo in the Republic of Gabon. Discovered in 1972, and unique to Gabon, these reactors operated for up to a million years, producing abundant energy as well as high level nuclear waste products (HLNW). Research has shown that organic substances in and near the natural reactors are mostly solid graphitic bitumen. Precursor to the solid bitumen was liquid bitumen, prolifically generated by organic matter-rich sediments in the 2.1 Ga year-old Francevillian Series of Gabon, and in the natural reactors themselves by hydrous reaction mechanisms prior to, during, and following criticality. The solid bitumen which encloses uraninite and fission generated isotopes entrapped in uraninite has effectively immobilized radiogenic nuclides and fission products in the reactors for hundreds of millions of years. With over four hundred nuclear power plants operating world wide, and as yet, no available long term HLNW repositories, safe disposal of HLNW is a very important and controversial issue in society. The Oklo analogue remains a viable option.

PRELIMINARY REPORT ON THE SUMMARY RESEARCH OF JURASSIC BLACK SHALE HOSTED MN-MINERALIZATION, ÚRKÚT BASIN, HUNGARY - THE ROLE OF MANGANESE IN MICROBIAL LIFE

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IGCP Project No.429 will create an important frame for international cooperation in the subject, Organics and Environmental Issues in the next five years.

Hungarian National Committee of IGCP supported this programme from the beginning as we think this is a very important and difficult field of interdisciplinary research.

From Hungary originally three research centers planned to join to the project, the Hungarian Geological Institute, the Environmental Microbiological Research Group and the Laboratory for Geochemical Research of the Hungarian Academy of Sciences.

The Hungarian Geological Institute besides the technical support plans to participate in the following topics:

- fossil fuel mining and environmental guidelines
- atmosphere as a transport mechanism for dissolved organic and inorganic particulates
- Ge-rich Eocene sub-bituminous coal waste disposal, and on fly ash of solid fuel power stations.

In the Laboratory for Geochemical Research the study on the black shale hosted Jurassic manganese deposit of Úrkút is going on.

In 1987 the black shale model in manganese ore formation at that time was the key to solve the problem of the hundreds of million tonnes of Mn-carbonate ore formation, which was successful.

The Hungarian national working group (M. Polgári, Z. Szabó), partly works now on the summary of the results of the Hungarian manganese research and mining of the last 80 years. Summarizing the data it seems that the conditions in the Úrkút Basin were more complicated than we thought earlier, the role of organics was more complex.

By now, it seems that in the Úrkút basin two little hydrothermal Mn-deposits were formed (in Eplony and in Csordahegy, Z. Szabo), where the morphological signs of primary bacterial activity can be supposed. On the other hand the marine organic matter (plankton)

which accumulated together with protore particules and other sedimentary matter had an important role in primary and later in secondary ore formation through degradation which took place during diagenetic processes. Their role can explain the heavy metal and rare earth elements distribution of the ore deposit which were earlier thought the result of terrigenous effect. One of the most important results based on data was summarized by M. Polgári, namely that the clay part of the black shale formation probably was originated from the weathering of volcanic glass in the Úrkút deposit, and the weathering took place together with Mn and Fe enrichment and the degradation of the high amount of organic matter. This very complicated geochemical system was influenced by the Toarcian oceanic anoxic event, which could be important in transporting Mn support, too. These processes resulted a very special character of clay formation. Cretaceous tectonic movements and secondary geochemical processes, and erosion partly or totally destroyed the original formation which created a very difficult situation for reconstruction of the primary situation.

To prove this phenomena needs further investigations. To understand the role of microorganisms and other effects we give a short summary on the role of manganese in microbial life (M. Kecskés). Manganese has a role for plant growth as an activator of many respiratory enzymes; involved in chlorophyll synthesis and in the photochemical reactions of photosynthesis. This role of action can be present in many algal groups as well. Manganese is naturally present in wood.

Manganese is the most abundant metal after Ca, K, Mg. The concentration of manganese is relatively high in wood (approximately 10 to 100 mg/kg dry wood), indicating that the availability of manganese during initial stages of wood decay is probably not a limiting factor in lignin degradation. It was observed that during white rot decay of wood the oxidation state and location of manganese change resulting in black spots of insoluble manganese oxides precipitates in decayed wood. Lignin degradation by *Penicillium chrysosporium* is a secondary metabolic event. One of the most important point that is manganese has a special role in ligninolytic peroxidase (three main types of extracellular oxidative enzymes; lignin peroxidase, manganese dependent peroxidase, and laccases) have been shown to be produced by white rot fungi which potentially participate in lignin degradation. Manganese is the essential cofactor of manganese dependent peroxidase. Manganese (III) generated by manganese dependent peroxidase acts as a mediator in the oxidation of various phenolic compounds. However, manganese (II) is implicated to play a role as cofactor of manganese dependent peroxidase in terms of completing the catalytic cycle. Manganese (II) is important for preventing the H₂O₂ inactivation of the enzyme.

Beside this, manganese has a role in nitrogen fixation and other microbial metabolism and other biogeochemical transformation in the nature.

Microorganisms are capable of oxidizing divalent manganese to tetravalent manganese. Various soil and aquatic bacteria and fungi carry out the oxidation of manganese. Some *Gallionella* species deposit manganese oxides within their sheath. It has been suggested, but not rigorously demonstrated, but manganese oxidation may support chemolithotrophic growth of some bacteria. The divalent manganese form also can be regenerated by microbial reduction. The removal of oxygen and the production of acids by facultative anaerobes favors the reduction of manganese. Some bacteria are able to use tetravalent manganese as an electron acceptor, replacing oxygen as the terminal electron acceptor in respiration, resulting in the production of divalent manganese. Microbial processes that reduce manganese increase the mobility of this element. Very important task to study the effect of environmental factors (including polluting materials, too) on microorganisms and their activities involved in manganese biogeochemical cycling.

ACID DRAINAGE: COMBINING FIELD STUDIES AND MODELLING

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Organic fossil fuels contain often pyrite, as the sedimentation under anaerobic conditions leads to the reduction of both Fe(III) and sulphate, with pyrite becoming oversaturated. During the mining activities, the pyritic material is brought into the connection with atmosphere. The result is active oxidation of pyrite and formation of acid leachate, commonly known as acid mine drainage (AMD) or acid rock drainage (ARD). The leachate contains often high concentrations of heavy metals, that were originally in the sulphidic form, or were adsorbed to the other solid phases of the source rock (for example bound with the organic matter). The deterioration of the surrounding environment depends mainly on the buffering capacity of the rocks and sediments the leachate is flowing through. If the buffering capacity is low, it becomes depleted and the leachate needs to be treated not to cause major regional scale problems.

The best way to prevent acid drainage problems is to foresee the oxidation processes especially through minimising the access of oxygen to pyrite. Ten grams of pyrite has a potential to produce 330 kg of pH=3 leachate. This reaction, however, requires availability of 1.9 dm³ of oxygen, that is usually not originally present in the system. Thus, pyrite oxidation often becomes rate limited by oxygen transport processes, such as diffusion driven by oxygen concentration differences, forced convection (wind blow) through the slopes, as well as free convection because of the convective air currents, formed in the slope areas. Using simple laws of physics, it is possible to quantify these fluxes and predict the rates of pyrite oxidation.

The oxygen access problem should have been solved before mining activities had been undertaken. Unfortunately, this has seldom been done and most of the countries are facing the acid drainage problems. Any remedial action, however, starts again with characterisation of the rates of pyrite oxidation, for example to understand, how much buffer is needed to neutralise the leachate. The tools to calculate pyrite oxidation rates are available, only the skills are needed to develop site-specific approaches.

The other problem of fossil fuel mining is co-existence of organic matter and pyrite. Pyrite oxidation leads to the temperature increase of several tens of degrees, with subsequent increased rates of organic matter oxidation and spontaneous combustion of the rocks. Specific geological or disposal conditions needed to satisfy the combustion criteria. Greater steepness of the slope, higher permeability and greater height of the waste rock dumps are the factors, usually increasing the probability of the waste rock to combust. The result is pollution of atmosphere. It should be noted, however, that spontaneous combustion eliminates pyritic acidity in the gaseous phase, in such a way decreasing the water pollution potential.

A site-specific approach has been developed to characterise and predict the changes in the pyritic waste rock in Maardu, Estonia. During the phosphate mining, the overburden including pyritic alum shale was dumped without paying attention to the pyrite and organic matter oxidation capabilities.

The results were earlier described formation of acidic drainage, as well as spontaneous combustion. Fortunately, the overburden contained also limestone, buffering the acidity. Although the main processes and fluxes have been well-defined, there is still an uncertainty in long term site pollution potential assessment because of the encapsulation of limestone lumps by gypsum and ferric oxyhydroxide precipitates. The other modelling result was, that

although the leachate is circumneutral (pH 7-8.6), it still contains sulphates considerably higher than drinking water standards, and the time scale of sulphate leachate production is about 1000 years with quantities of about 3 million tonnes of polluted leachate per year.

It is believed that the detailed Maardu case study helps to develop site-specific approaches for different cases, as every site has individual character. During the IGCP 429 project, the cooperation is sought to carry out parallel field and modelling studies, or model the existing data to get both the better overview of the role of pyrite in fossil fuel weathering process and give guidelines for the prevention and remediation techniques.

The field trip during the IGCP 429 inaugural meeting already introduced to the participants the acid drainage problems in the Czech Republic. The participants are encouraged to gather and present information for the site-specific problem analyses. The guidelines how to do it will be provided during the first months of 1999. One of the major goals of the acid drainage group is to find the best ways for site assessment and choice of remediation technologies.

ORGANIC MATTER IN SOME CHARACTERISTIC ENVIRONMENTS IN THE REPUBLIC OF MACEDONIA

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The issue of the examination of organic matter in individual environments in the Republic of Macedonia has not been given sufficient consideration and attracts great attention. There are numerous localities in the country with high concentrations of organic matter, particularly in the terrains with established coal deposits. Attention should also be paid to organic matter present in soils particularly to those in close proximity to the dwelling places. Special challenge in this regard are the terrains in the vicinity of open pit coal mines and premises for technological modelling.

Generally viewed, we can speak of three characteristic environments in the territory of the Republic of Macedonia in which high amounts of organic matter can be found.

The first consists of organic matter established in bituminous shales near the village of Plesenci (the town of Probistip). It covers an area of some 2 km² in which Neogene sediments prevail, the series of bituminous shales reaching the very surface. The topmost portions of the cross-section also contain humic composition overlying a series of sand overlying, in turn, bituminous shales in several heterogeneous 5 m thick layers. This producing series is underlain by sandstones and tuffs. The bituminous shales possess fairly constant composition with ashes amounting to 65 to 86% of the total mass. The heat value amounts to 3069 KJ/kg, the total moisture amounting to 7- 20%.

The second type consists of organic matter within the quartz-graphitic schists in the Sasa - Toranica Pb-Zn area (Eastern Macedonia). It is a producing quartz-graphitic series intercalated by cipolines affected, later, by hydrothermal activity ensuing skarns with high percentage of Pb-Zn mineralization. Detailed examinations of the organic matter in the quartz-graphitic schists have not been conducted, but their presence in the schists is well known. The presence was also indicated by the results of examinations carried out on sulphur and carbon from the pyrites and calcites.

The third type consists of organic matter inside and around the open pit coal mines (lignite) such as those in Suvodol (Bitola), Brik (Berovo), Oslomej (Kicevo), etc. Concrete

data about the contents of organic matter in coal and soils around the open pit mines have been obtained and will be presented in future papers.

THE APPLICATION OF COMPOUND-SPECIFIC-ISOTOPE-ANALYSIS FOR TRACING ORGANIC SUBSTANCES THROUGH THE EARTH'S ENVIRONMENT

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At the Department of Earth Sciences of the University of Lausanne (IMP-UNIL) a new laboratory to study chemically and isotopically organic substances has been set up. This laboratory houses the instrumentation for extraction, fractionation and analyses by gas chromatography - mass spectrometry (GC-MS) and gas chromatography - combustion - isotope ratio mass spectrometry (GC-C-IRMS) of organic substances in rocks, sediments, soils, plants, waters and aerosols. These facilities are presently fully operational for using the novel technique of compound specific isotope analysis (CSIA) as a mean to trace the origin, potential sources, preservation/ degradation (diagenesis and metamorphism) and fate of organic chemicals (natural or synthetic) through the earth's environment. In addition, the molecular organic geochemistry combined with the already existing geochemical-isotopic tools for water, soil, rock, and mineral analyses (vacuum lines, elemental analyzer, laser-ablation extraction, IRMS for δD , $\delta^{13}C$, $\delta^{18}O$, $\delta^{15}N$, $\delta^{34}S$ measurements) allows the IMP-UNIL to undertake research programs in a broad spectrum of environmental issues, including studies of recent and ancient organic matter and studies of organic and inorganic pollutants in terrestrial and aqueous systems.

Three case-studies from the main stages of biomass-recycling in the atmosphere, hydrosphere, terrestrial environment and geosphere will be presented:

Short lived biomass: "Characterization of olive oil by carbon isotope analysis of individual fatty acids: implications for authentication and paleoclimatological changes in the Mediterranean Basin".

Fatty acids are main constituents of plants, trees, grasses, phytoplankton and are in a continuum and dynamic chemical and isotopic equilibrium with the atmospheric carbon dioxide. These carbohydrates and their derivatives are the main constituents of dissolved organic matter and may be suitable molecular markers for anthropogenic and early diagenetic processes. The ecological importance of the lightly biodegradable fatty acids and oleochemicals will be stressed in ongoing IMP projects.

Long lived biomass: "Origin and fate of organic matter in Lake Léman (Lake Geneva), Switzerland/France deduced from stable isotope analyses of individual lipids".

Lake Geneva is the largest natural lake in central Europe, and it is the most important water source for a highly populated region of Switzerland as well as the border cities of France. The lake water is used for domestic, industrial and agricultural purposes. Understanding organic matter pathways is complicated by the numerous sources and chemical changes that occur in the water column and recent sediments. We intend to determine the sources and fates of natural and anthropogenic organic matter inputs to the lake by using

CSIA ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) of different lipid fractions. The natural organic sources (e.g., macrophytes, phytoplankton, algae, wind-transported terrestrial plant debris) and potentially toxic organic compounds from anthropogenic activities (e.g., domestic and industrial waste-waters, fossil fuel burning, oil seepage) will be characterized and apportioned in the water and recent sediment column. Information relating to the relative contributions of these organic sources is important to our understanding of the structure and functioning of the drainages in the lacustrine ecosystem, and will allow us to correct potentially damaging environmental problems.

Fossil biomass:

”Geochemistry of the organic mineral *evenkite* from septarian concretions in the Oxfordian (Upper Jurassic) marls of the French Alps - Implications for preservation of organic substances”.

“Archaean Witwatersrand Basin, South Africa”

ACTIVITIES RELATED WITH SOME OF THE TOPICS OF THE IGCP 429 PROJECT ”ORGANICS IN MAJOR ENVIRONMENTAL ISSUES” AND CONTRIBUTION POSSIBILITIES

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Activities of possible interest related with some of the topics of the IGCP 429 project ”Organics in major environmental issues” which can be included, are subdivided into two major fields and summarised as follow:

1- Activities of research related with the study of the mobilisation and leaching of some potentially dangerous trace elements from refuse and wastes of different origin. As an example, in Northern Spain, several centuries of coal mining activities have generated a significant amount of waste and refuse from mining and coal extraction, coal cleaning processes and even now, ashes from coal combustion. Coal refuse, mainly that derived from coal mining and extraction is in part used as a raw material in construction industries and civil engineering, in agriculture and even when it has a relatively high coal content, it is used in combustion processes. However, the excess of this waste is placed in disposal sites such as lagoons, mounds, landfill sites and dumpsites. This waste is made up of considerable inorganic fraction and a variable organic fraction. The organic fraction is lower than 40,0% vol. of the total while the inorganic fraction has a variable mineralogical composition and represents between 94,0% and 60,0% of the total. The sulphur content, mainly of a pyritic character, is between 0,5 and 2,0% (dry basis). Moreover, it is known that coal waste contains trace elements in different concentrations such as : As, Cd, Cr, F, Hg, Ni, Pb, Se, etc... which can react and solubilize under weathering conditions and are a source of potential pollution of surface and subsurface waters. So, an important activity which could be included in the IGCP 429 project is research on prediction of the environmental impact of different wastes on disposal sites in relation with their characteristics and trace element content and the leaching behaviour of these trace elements under different conditions.

2- The second type of activities also related with topics of organics in the field of environmental issues, includes research and services of an immediately applicable character. These activities are intended to help and advise industries, enterprises and organisms for environmental control. Also of importance are the detection, identification, classification and

quantification of pollutant organic particles, of different origin, such as coal using and transformation, (fly ashes and chars from coal combustion) and graphite particles, that form a part of a programme of elimination of pollution in estuaries, beaches, rivers and in general contaminated areas. Another important concern activity in this field is also the control of dumping of materials derived from industrial processes or mining.

The above mentioned activities are in part related with the topics and tasks proposed in the IGCP 429 project such as the analysis of organic/inorganic interaction for environmental applications and the weathering processes of fossil organic matter and associate sulphides (in which activities from point number 1 can be included). The study of regional and geochemical effects of the organic matter such as fly ash, bottom ash, etc., and the improvement of methods that lead to the identification of potentially dangerous atmospheric particles (reported in the second point) are also considered.

INFLUENCES OF ANTHROPOGENIC ORGANIC MATTER IN AGRICULTURAL: HUMIC SUBSTANCES AND pH EFFECTS ON CLAY DISPERSION AND HYDRAULIC CONDUCTIVITY

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In arid and semi-arid zones shortage of water is a major problem. In Israel reclaimed wastewater is used as a substitute for fresh water for some crops. Today 25% of the water in agriculture is reclaimed wastewater, and the proportion is increasing. The use of effluents, together with the increased use of sewage sludge, municipal solid waste and agricultural waste has increased the input of anthropogenic organic matter to the soils. On the other hand, agriculture will be the solution for eliminating liquid or solid waste with minimal environmental problems. The research includes several topics:

1. Characterization of organic matter and humic substances (HS) in soils, waste and water.
2. Development of extraction methods of HS from soils, wastewater and organic waste.
3. Characterization of composting processes of organic waste (agricultural and municipal waste-MSW) and enzymatic reactions.
4. Study of the effects of humic substances on soil:
 - Flocculation and soil structure.
 - Changes in the composition of HS as a result of intensive addition of anthropogenic organic matter.
 - Interaction between HS and boron.
 - Humic substances and mobilization of heavy metals.
 - Humic substances and increased growth response.

The influence of HS on clay flocculation and the hydraulic conductivity of soils was discussed. HS are important factors in soil particle associations. Flocculation and dispersion characteristics of homoionic montmorillonite were studied as a function of exchangeable cation (Na^+ and Ca^{2+}), humic acid (HA) and fulvic acid (FA) concentration (0-40 mg L^{-1}), and pH (4, 6, 8 and 10). Flocculation Values (FV) of Na-montmorillonite increased with increasing concentrations of HS at all pH levels. For pH values of 4, 6 and 8, a sharp increase in FV was observed with increasing HS concentration up to 10 mg L^{-1} (37.5 g kg^{-1} clay). Only slight increases in FV were observed for HS concentration > 10 mg L^{-1} at these pH values. In contrast, for suspensions at pH 10, HS concentrations up to 10 mg L^{-1} had little effect on the FV, but further addition of HS caused an increase in FV up to 141 mmol L^{-1} . In contrast to Na-montmorillonite suspensions, addition of Ca-humate or Ca-fulvate to Ca-montmorillonite had no effect on the FV. The effect of HS on the stability of Na-montmorillonite suspensions is explained by interactions between negatively charged HS molecules and the edge charge of the

clay. These interactions are affected by pH and by the charge and configuration of the HS macromolecules. In pure clay systems at pH values below the point of zero charge (PZC) of edge sites, edge-edge (E-E) and edge-face (E-F) interactions among clay platelets are the dominant flocculation mechanisms. At pH values above the PZC of the edge sites, only F-F associations occur. In the presence of HS at pH values below the PZC, negative HS molecules are adsorbed to positive edge sites causing edge-charge reversal (from positive to negative). Consequently, increased electrolyte concentrations are required for flocculation relative to Na-montmorillonite suspensions without HS. The second flocculation mechanism we propose is based on a random distribution of the HS macromolecules among the montmorillonite tactoids. The FV of such a mixture is higher than the FV of montmorillonite suspensions. The term *mutual flocculation* (heteroflocculation) has been suggested to describe this mechanism.

In further research, the influence of dissolved organic matter (DOM) contained in reclaimed wastewater effluents (mainly humic substances) on the flocculation of montmorillonite and on the hydraulic properties of soils was studied. Flocculation values (FVs) for Na-montmorillonite increased with increasing concentrations of DOM at all analyzed pH levels (5.5, 7.0 and 8.5). Maximum FV levels were exhibited for Na-montmorillonite at the highest DOM concentrations. The effect of DOM on FV can be explained by the mechanisms of *edge-charge reversal* and/or *mutual flocculation*. The hydraulic conductivity (HC) of a sandy soil was determined in the laboratory, by leaching columns with an electrolyte solution chemically similar to that of the wastewater effluent (but without DOM). In columns treated with wastewater effluent, HC exhibited a sharp decrease to only 20% of its initial value. The adverse effect of DOM on HC was evident for this soil despite a relatively low exchangeable sodium percentage (ESP). The reduction in HC is likely to be the result of decreased soil pore-size, which reflects two processes: (i) retention of part of the DOM during water percolation; and (ii) a change in pore-size distribution due to swelling and dispersion of clay particles. The latter could result from a higher percentage of adsorbed sodium combined with the presence of humic substances from the wastewater effluent.

FAVOURABLE PREMISES FOR THE RECLAIMING OF SOILS FROM AREAS AFFECTED BY THE EXPLOITATION OF THE PLIOCENE COALS FROM OLTENIA (ROMANIA)

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Begun in 1967, the intensive coal exploitation from the pliocene coal-generating basin of Oltenia, placed in the south-west of Romania, has produced a lot of modifications on the environment. In Oltenia there are 21 mining exploitations in quarries where it were dislocated billions of tons of dump rock which were stored either in internal wastes or outside the quarries, in external wastes. Some of these wastes were rearranged and restored in the agricultural and forest circuit, but this proceeding was applied only in some cases, the storage and the redistribution of the soils being very expensive.

We try to establish that the petrographical and chemical nature of the constituted rocks and the intercalations between the coal beds in Oltenia, have an important role for the plants development.

In Oltenia pliocene coals basin, because of the relatively low degree of carbonification (lignite stage), in the argillous coals and in the coaly clays, there are free humic acids, fact which constitutes one of the most important premise for their using for the fertilizing of the agricultural surfaces on wastes.

The humic substances role is essential for the soil, they contribute to:

- the formation of the soil structure units, permitting their loosening and, implicitly, the

- water
and air circulation;
- the restraint of the water because their hygroscopical properties;
 - the transformation of some insoluble substances into soluble substances which have elements assimilated by the plants and indispensable for their different physiological functions;
 - the increasing of the soil CO₂ content, which contributes to the plants development;
 - the facilitation of the phosphorus assimilation and of the increasing of the nitrogen content;
 - the stimulation of the chlorophyllian assimilation and the increasing of the plant absorbing power for the mineral substances.

All these properties of the humic substances explain why the dust of the low degree carbonification coals determines the increasing with 24-55% of the cereal crops quantities and the fact that in the experimental agricultural stations situated on the coal wastes of Oltenia it obtain abundant crops for a large series of plants.

Another important premises for the reclaiming of the agricultural destroyed and degraded lands, are the contents of P₂O₅ and K₂O from the clays of the coal intercalations which are comparable with others soils from Romania (in some places the P₂O₅ contents are between 7-10%).

Some results of the chemical analyses for AH^{daf}, P₂O₅ and K₂O for some lithotype and waste dump samples are given in the following table:

Quarry (waste dump)	Lithotype	AH %	P ₂ O ₅ %	K ₂ O %
Lupoiaia	clay	1,36	0,14	1,96
Lupoiaia	clay+coal	5,85	0,15	1,90
Lupoiaia	clay+coal	-	0,14	1,90
Lupoiaia	soil +coal	2,14	0,14	1,76
Lupoiaia	clay	0,46	0,14	2,22
Lupoiaia	clay+coal	2,46	0,15	2,24
Lupoiaia	clay+coal	-	0,19	1,87
Lupoiaia	clay+coal	3,74	0,15	2,00
Lupoiaia	clay+silt+coal	5,91	0,16	1,76
Lupoiaia	clay+silt+coal	2,25	0,15	1,96
Rosia	clay+sand	0,46	0,18	2,83
Rosia	clay+coal	0,06	0,15	2,57
Rosia	clay+coal	0,69	0,16	2,35
Rosia	clay+coal	2,45	0,15	1,88
Rosia	clay	0,40	0,17	2,55

Quarry (waste dump)	Lithotype	AH %	P ₂ O ₅ %	K ₂ O %
Rosia	clay+sand	1,04	0,17	1,75
Poiana	clay+coal	2,25	0,14	2,20
Poiana	clay+sand	0,18	0,11	2,05
Poiana	clay+coal	-	0,15	2,87
Poiana	weak sandy clay	0,89	0,19	2,18
Tismana	sandy clay	-	0,08	3,17
Tismana	sandy clay	0,43	0,08	3,26
Tismana	clay+sand	1,58	0,08	2,98

Lupoiaia	sand	0,06	0,08	1,55
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Also, the trace elements, either in the ash of the coals or in the clays mixed with coal fragments, have a special importance in different biological processes of the plants life: diverse synthesis (chlorophyllian, of the glucides, of the protides) and respiration, growth, defense, fructifying, and other processes.

The variability limits for the trace elements content from these samples, are:
 Zr : 100-250 ppm; Cu: 35-75 ppm; Pb: 15-60 ppm; Sn: 3-15 ppm; Mn: 450-2200 ppm;
 Ga: 10-30 ppm; Cr: 50-125 ppm; Ni: 30-80 ppm; V: 55-95 ppm; Zn: 80-200 ppm;
 Ti: >3000 ppm; Co: 8-35 ppm.

It is required the implementation of some interdisciplinary researches in which must be involved geologists, chemists, soil specialists, agronomists, to establish the best networks for the producing of unconventional soils (antropic protosoils) obtained from the lithotypes which are the result of the coals quarry exploitation, inclusively a small part of the extracted coals and their ash.

These antropic protosoils should resolve not only the reclaiming of the agricultural and forest lands degraded or destroyed by the coal exploitations, but also the ones affected by the erosion or degraded by the intensive agricultural exploitation; also, there is the desertification risk of great surfaces submissive to the irrational cutting of the trees and to the forest protection curtain elimination.



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