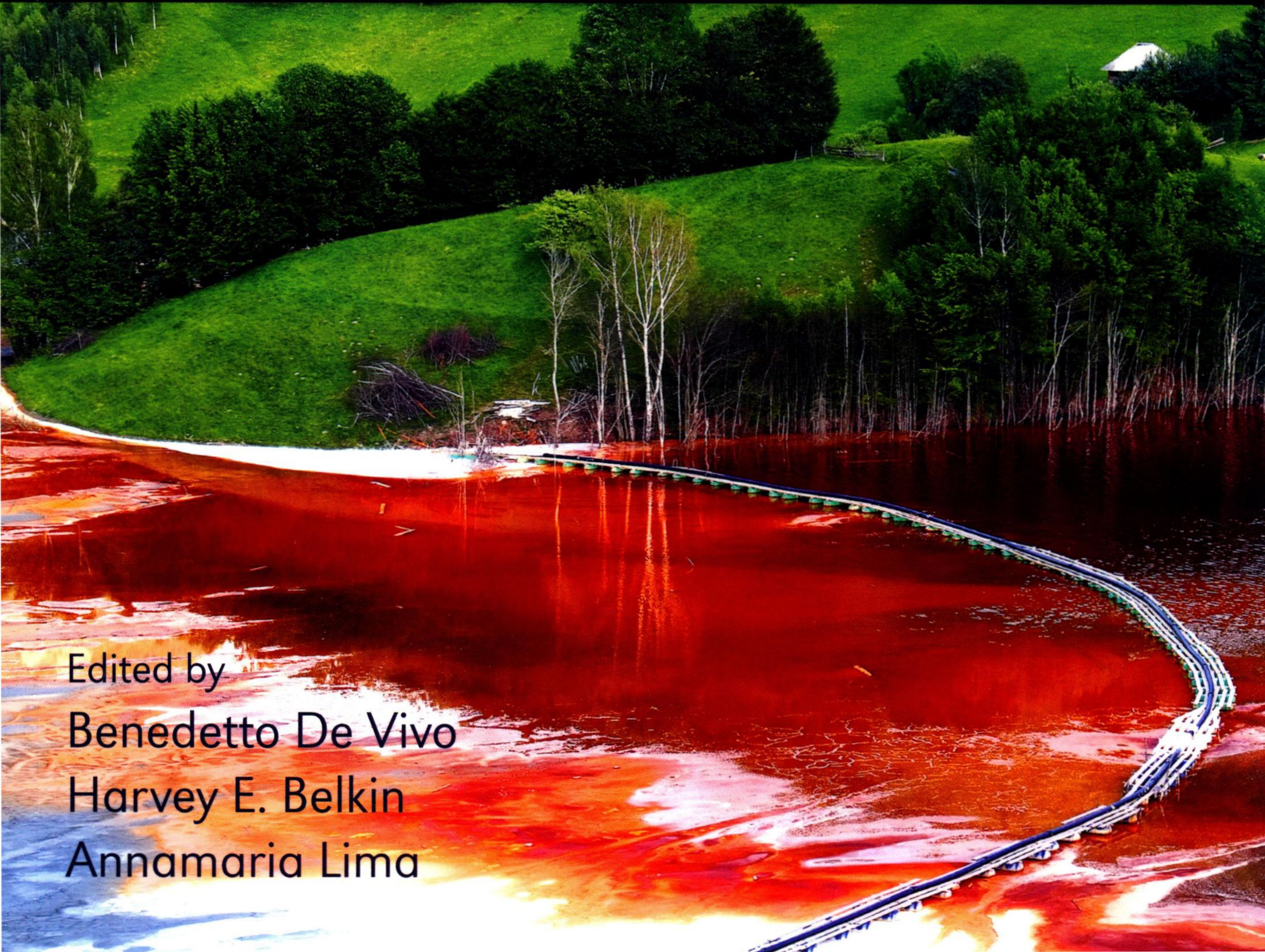
Second Edition

Environmental Geochemistry

Site Characterization, Data Analysis and Case Histories



Edited by
Benedetto De Vivo
Harvey E. Belkin
Annamaria Lima

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Overview of the field of Environmental Geochemistry, including current site characterization and data analysis techniques

Environmental Geochemistry 2e reviews the role of geochemistry in the environment in general as well as detailing state of the art applications of these principles in the field, specifically in pollution and remediation situations. Chapters cover both philosophy and procedures, as well as applications, in an array of issues in environmental geochemistry including health problems related to environment pollution, waste disposal, and database management. This updated edition also includes illustrations of specific case histories of site characterization and remediation of brownfield sites.

Key Features

- Covers numerous global case studies allowing readers to see principles in action
- Explores the environmental impacts on soils, water, and air in terms of both inorganic and organic geochemistry
- Written by a well-respected author team with over 100 years of experience combined
- Includes updated content on: urban geochemical mapping, chemical speciation, and characterizing a brownfield site

About the Editors

Benedetto De Vivo studied at the University of Napoli Federico II and graduated from there in geological sciences. After graduation, he worked as consulting geologist for private companies operating in Italy, Africa, and Central America in the field of ore deposits, geochemical prospecting, environmental geology, and hydrogeology. Later, he was an associate professor in applied geochemistry at University of Napoli Federico II, and in 2000 he became a full professor in geochemistry at the same university. He has been the Editor in Chief of the Journal of Geochemical Exploration (JGE) (2007–2016), and is now co-Editor in Chief of Geochemistry: Exploration, Environment, Analysis (GEEA) (The Geological Society of London).

Harvey Belkin for almost 50 years had been with the USGS as a research geologist whose work focused on geochemistry. Most recently he had been the project chief of the Reston Microbeam Facility, where they created a baseline of chemical and textural properties of mineral species—specifically on halogens, HAP's, elements, or rare earth elements and a project leader on a program focusing on the geochemistry of solid fuels, specific as it relates to coal in China.

Annamaria Lima is an associate professor in geochemistry in addition to being a member of the Editorial Boards for the journal Geochemistry: Exploration, Environment, Analysis. She also lectures at UNIA (Spain) on environmental geochemistry. Her research includes: geochemical exploration for mineral resources, both from an exploration perspective as to identify the potential environmental hazards which can relate to these activities; environmental geochemistry for evaluation of anthropogenic pollution, site characterization, and remediation; fluid and melt inclusions in minerals: applied to ore deposit genesis, geothermy, magmatology, and volcanology.

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ENVIRONMENTAL GEOCHEMISTRY

SITE CHARACTERIZATION, DATA ANALYSIS AND CASE HISTORIES

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Preface

The first edition of the volume *Environmental Geochemistry: Site Characterization, Data Analysis, Case Histories* contained selected papers presented at the "Workshop: Environmental Geochemistry—Site Characterization, Waste Disposal, Data Analysis, Case histories" held in Napoli (Italy) on May 4–5, 2006. Participants represented private and public institutions from Canada, Finland, Greece, Italy, the United Kingdom, and the United States. The theme of the original workshop was multidisciplinary methods of characterizing contaminated sites using modern geochemistry with examples from different countries in Europe, North America, and Asia. Special themes included soil, surface and groundwater contamination, environmental pollution and human health, and data interpretation and management.

It is especially appropriate that the first edition of this volume was completed in 2007, as it was the hundredth anniversary of the birth of Rachel Carson. Rachel Carson published *Silent Spring* in 1962, which brought environmental concerns to an unprecedented portion of the American public and the world in general. *Silent Spring* spurred a dramatic reversal in US national pesticide policy, leading to a nationwide ban on DDT and other pesticides, and the grassroots environmental movement it inspired led to the creation of the United States Environmental Protection Agency and other similar agencies. Now, we are in a situation where the methods and techniques of remediation are developed with a greater understanding of the baselines and economics of the applied clean-up processes. Remediation of the polluted sites must be accomplished within budgets of the communities together with the rigor of science.

For this second edition, many chapters of the first edition have been updated by the authors. In addition, new chapters introduce more case histories, including examples from health issues to the contamination and remediation of industrial sites, showing the great variety of environmental problems where geochemistry is involved. This enables a wider approach to the environmental problems from a geochemical point of view.

Environmental geochemistry has relationships with a wide range of other sciences. Seldom are the environmental problems purely geochemical, but solving them requires cooperation with other sciences. On one hand, environmental geochemistry establishes and explains links between the natural or disturbed chemical composition of the earth's surface and the health of plants, animals and people. At the same time, we cannot forget social and economic issues caused by disturbance of the geological balance of element concentrations in the surficial deposits. At the other end we have engineering sciences dealing with such phenomena as karst problems or developing methods for remediation of contaminated land.

Beneficial elements regulate or promote enzymatic and hormonal activity, whereas other elements may be toxic, or both may occur, as a function of dose. Bedrock geochemistry controls the composition of soil and hence that of water and vegetation. Environmental issues, such as pollution, arising from the extraction and use of mineral resources have an influence on the living conditions of humans and other biota. Geochemical surveys of soils, water, and plants show how major and trace elements are spatially distributed. Associated epidemiological studies reveal the possibility of causal links between the natural or disturbed geochemical environment and disease. Experimental research illuminates the nature or consequences of natural or disturbed geochemical processes.

The wide range of topics from the viewpoint of health is stated in the journal *Environmental Geochemistry and Health*: "The journal particularly welcomes novel research linking environmental geochemistry and health issues on such topics as: heavy metals (including mercury), persistent organic pollutants (POPs), and mixed chemicals emitted through human activities, such as uncontrolled recycling of electronic-waste; waste recycling; surface-atmospheric interaction processes (natural and anthropogenic emissions, vertical transport, deposition, and physical-chemical interaction) of gases and aerosols; phytoremediation/restoration of contaminated sites; food contamination and safety; environmental effects of medicines; effects and toxicity of mixed pollutants; speciation of heavy metals/metalloids; effects of mining; disturbed geochemistry from human behavior, natural or man-made hazards; particle and nanoparticle toxicology; risk and the vulnerability of populations, etc." In addition to the health problems, contamination of soils and waters cause serious social and economic influence/problems. Overpopulation at the seaside and in the areas of big cities contaminates soils and waters. Water pollution forces populations to find new areas for living. Costs of cleaning contaminated soils and waters are enormous. On the other hand, remediation of contaminated soils and waters creates new industry and needs new innovations from scientists.

The focus of geochemists has almost exclusively been on providing evidence, but not specifically on offering solutions for environmental problems. Geochemists produce geochemical information that is valuable for environmental legislation, but the solutions of social problems often demand debate with political decision makers. The geochemical information must be integrated with social, engineering, and economic factors. We strongly encourage geochemists to increase their activities in these issues.

From the geological point of view, *Geoenvironment Newsletters* classified the environmental problems as follows:

- Earthquakes
- Volcanism
- Mass movement
- Flooding
- Erosion
- Sedimentation
- Land subsidence
- *Land deterioration*
- *Problem soils*
- *Soil contamination*
- *Resources Depletion*
- *Water pollution*
- Miscellaneous problems

This list shows the wide range of environmental problems just from the geological point of view. The five last issues in the list include a strong geochemical component. Thus we can say that the role of geochemists in solving environmental problems is essential. Other sciences such as medicine, biology, agriculture, and many others deal with other types of environmental problems. Furthermore, geochemistry has an essential role not only in geoenvironmental problems, but it can also successfully contribute to solving environmental problems together with other sciences.

The EU Commission has made its own list of environmental problems (http://ec.europa.eu/

environment/soil/index_en.htm) from the political point of view:

- *loss of organic matter*
- compaction
- *salinization*
- landslides
- *contamination*
- soil sealing

This kind of list can easily be continued. But again, geochemistry plays an essential role in most of the issues indicated in this list. Soil is, however, increasingly degrading, both in the EU and at a global level. Erosion, loss of organic matter, compaction, salinization, landslides, contamination, sealing, etc., all have negative impacts on human health, natural ecosystems and climate, as well as on our economy.

The major sources of anthropogenic chemicals and toxic materials into the natural environment can be found in various industries, including mining. Even more contamination is caused by traffic, agriculture and from domestic use. Increasing population of humans and increasing living standards produce increasing amounts of wastes and as they are concentrated in rather restricted areas, the problems accumulate. Development of legislation has restricted the growth of emissions from industry and traffic. However, despite the fact that industry has done much to restrict emissions of harmful elements, a clean industry is still far in the future and in many places the old emissions and industrial wastes are still found in surface soils. Emissions from traffic have not decreased because of their increasing numbers, but we can assume that cleaner vehicles will be a reality in the future. In many countries agriculture is the main source of pollution. Growing population needs increasing amounts of food and more effective methods of agricultural production. Agriculture uses different kinds of chemicals, which, compared to industrial or vehicle emissions, are often much more complicated in their distribution and effects on biota.

Earlier, decisions to remediate contaminated land were based on different action limits defined in environmental legislation. However, the natural geology varies much from place to place and causes different behavior of pollutants and their toxicity to humans and animals. Therefore, during the last few years, a risk assessment-based management protocol has been developed in many countries. In Finland, e.g., a Government Decree on the Assessment of Soil Contamination and Remediation needs (214/2007) came into force in 2007. It defines that the assessment of soil contamination shall be based on a site-specific estimate of the risks to human health and the environment. The contamination assessment should take into account the concentrations, total amounts, properties, and locations of harmful substances in the soil deposits. Natural geogenic background concentration levels as well as current geochemical baseline values should be taken into account when assessing potential contamination and the need for remediation. This takes into account that the natural geogenic element concentrations are, in many cases, at such a high level that they may cause problems related to human health. The environmental legislation sets rules regarding how to manage environmental problems. In the United States a common legislation conducted by USEPA covers the whole country. In Europe the situation is much more complicated. After serious discussions during the past 20 years, the EU Water Framework Directive was agreed on, but discussions on a Soil Framework Directive never reached a result which could have been accepted by all countries. The opinions of different interest groups were too diverse. This, on the one hand, shows the important role that soil is playing in modern societies. Thus in Europe, soil is not subject to a comprehensive and coherent set of rules in the Union. Existing EU policies in areas such as agriculture, water, waste, chemicals, and prevention of industrial pollution do indirectly contribute to the protection of soils. But as these policies have other aims and scope of action, they are not sufficient to ensure an adequate level of protection for all soils in Europe. The environmental legislation functions on a national basis resulting, e.g., in different action limits for the pollutants in the contaminated soils and waters, and only a few EU Member States have specific legislation dealing with soil protection.

The continued unsustainable use of soils is compromising the European Union's domestic and international biodiversity and climate change objectives. For all these reasons, the Commission adopted a Soil Thematic Strategy [COM (2006) 231] on Sep. 22, 2006 with the objective to protect soils across the EU. While the Commission in May 2014 decided to withdraw the proposal for a Soil Framework Directive, the Seventh Environment Action Programme, which entered into force on Jan 17, 2014, recognizes that soil degradation is a serious challenge. It provides that by 2020 land be managed sustainably in the Union, soil be adequately protected and the remediation of contaminated sites be well underway and it commits the EU and its Member States to increasing efforts to reduce soil erosion and increase soil organic matter and to remediate contaminated sites (http://ec.europa.eu/environment/soil/index_en.htm).

However, despite the EU Seventh Environment Action Programme, it still seems that different interest groups are far from a common understanding concerning the content of the EU Soil Framework Directive. On one hand, contaminated land poses huge economic risks for its owners; on the other hand, a big new industry could be created for remediation of contaminated land; and the third party consists of the "green" people who demand cleaning all contaminated land. Therefore, it is probable that European countries will continue managing contaminated land according to their national legislation. The national legislation, e.g., the action limits, differs greatly from country to country.

This book combines the important features of environmental geochemistry in 23 chapters. The methodologies applied in environmental geochemical studies are introduced in 13 chapters. Ten chapters concentrate on very practical problems, which are especially relevant and important to the preceding discussion. The case studies describe a variety of specific environmental problems, which in most cases are successfully solved but sometimes have remained unsolved.

Field work is the first step in geochemical studies and thus it forms the basis for a successful study. Field methodologies are discussed in five chapters.

Reijo Salminen summarizes experience from a number of recently completed regional scale studies showing briefly the most essential issues to be taken into account in planning and carrying out geochemical surveys in the field. **Swyngedouw *et al.*** provide an overview of sampling grids applied in soil studies, sampling bias, and sampling errors with some practical advice for sample handling and shipping. **Trick *et al.*** discuss groundwater sampling with a special emphasis on quality assurance. They also show how on-site measurements, such as pH, EC, dissolved oxygen, temperature, and alkalinity, can be used to provide a check for subsequent laboratory analyses. **Johnson *et al.*** compiles experiences from their collection of drainage sediment samples from active stream channels in Great Britain. They also introduce the geochemical baseline based on stream sediment and waters. The authors give detailed sampling protocols and discuss sampling strategies and equipment. **Qu *et al.*** summarize the principles of passive air samplers (PAS) techniques and progress of the polyurethane foam-based PAS (PUF-PAS) in monitoring persistent organic pollutants (POPs) from a local to global scale. They also illuminate the atmospheric transport of organochlorine pesticides (OCPs) from plain to mountain, as well as to demonstrate the feasibility of using PUF-PAS for achieving spatially and seasonally resolved data for POPs.

Chemical analysis of the collected samples produces the necessary data for interpretation of the results. Some special features of analytical methodologies are discussed in four chapters.

Swyngedouw and Lessard introduce gas chromatographic methods of chemical analysis of organic compounds with a special emphasis on quality assurance. The paper provides a procedure to extract, isolate, concentrate, separate, identify, and quantify organic compounds, including also important information on collection, preparation, and storage of samples. **Adamo and Zampella** introduce chemical extraction procedures that have been more widely applied to determine the plant and the human bioavailability of potentially toxic metals (PTM) from contaminated soil and their presumed geochemical forms. They show how crucial it is to establish the speciation, mobility, and biogeochemistry of the contaminants. Examples of complementary use of chemical and instrumental techniques and applications of PTMs speciation for risk and remediation assessment are illustrated. **Di Bonito and Young** discuss the importance of a complete chemical analysis of soil pore water, which represents a powerful diagnostic tool for interpretation of many soil chemical phenomena relating to soil fertility, mineralogy, and environmental fate. They describe in detail some of the current methodologies used to extract soil pore water. In particular, four laboratory-based methods, (i) high speed centrifugation-filtration, (ii) low (negative-) pressure Rhizon™ samplers and passive diffusion samplers, (iii) high-pressure soil squeezing, and (iv) equilibration of dilute soil suspensions and diffusive gradients in thin-films (DGT), are described. **Jiang *et al.*** give an overview on general techniques for microbial analysis in contaminated targets. They describe traditional and prevalent nucleic acids-, proteins-, and lipids-based technologies to study microbial abundance and diversity with emphasis on their underlying principles, major experimental procedures, and major disadvantages/advantages specific to different applications.

Several methodologies for *data processing* are developed to help the research. Techniques applied in processing environmental geochemical data are introduced in four chapters.

Johnsson *et al.* review the quality assurance methods developed in the British Geological Survey during 40 years work on regional geochemical mapping. The verification, quality control, and levelling processes are necessary to make data fit for the purpose for which it is to be used. **Annamaria Lima** discusses geochemical background values based either on statistical frequency analysis or spatial analysis. She illustrates the application of GeoDAS™ software to perform multifractal inverse distance weighted (MIDW) interpolation and a fractal filtering technique, named spatial and spectral analysis, or simply the (S-A) method, to evaluate geochemical background at regional and local scale. **Di Bonito *et al.*** outline the development of geochemical modeling over time and its basic principles. They describe the state-of-the-art ion-binding and surface complexation models presently available for dissolved and particulate organic matter, mineral oxides of aluminum, iron, manganese, and silica and clay minerals. They present practical applications of these models and the most recent developments in biogeochemical modeling to link metal speciation to bioavailability, biotic accumulation and toxicity. Local scale *geochemical mapping* is the topic of **Albanese *et al.*** who discuss the main considerations necessary to undertake urban mapping activities in terms of planning, sampling, chemical analyses, and data presentation. In this context, modern geographical information systems (GIS) represent an indispensable tool for better understanding the distribution, dispersion, and interaction processes of some toxic and potentially toxic elements.

Contamination of soils and waters in the surroundings of industrial sites together with respective remediation methodologies are discussed in six chapters.

Ayuso and Foley have studied the application of Pb isotopes in monitoring anthropogenic contaminants in near-surface environments. Their results show that the contamination of industrial lead and consumption of fossil fuels are implicated in the waters from the regional wells in wide areas. **Cynde Sears** introduces a success story on how a site of a former power plant was changed into a multiuse recreational area. The site was heavily contaminated with polychlorinated biphenyls (PCBs), arsenic, and a wide range of petroleum hydrocarbons. Over a period of 26 years, the Town successfully gathered the financial, technical, and community resources it needed to remediate the site. The remediated area benefits the Town today, reflecting a true success story in the US effort to convert brown fields into productive use. **Qi *et al.*** introduces briefly the origin and environmental chemistry of organochloride pesticides (OCPs) and reviews the history and presence of OCPs in soils in China. They also document cases on OCPs distribution and influencing factors in Chengdu Economic Region in Sichuan Province, and Zhangzhou in Fujian Province, southwest and southeast of China, respectively. The majority of OCPs are not currently used POPs, but instead are remnants from earlier use. **Govil and Krishna** introduce studies on contaminate land areas in Katedan Industrial Development Area, Hyderabad, Telanga State, India. Soils, sediments, surface water, groundwater, lake sediments, and dump sites were studied for toxic metals with a special emphasis on their migration routes. **De Vivo and Lima** introduce the large remediation project of the heavily contaminated Bagnoli (Napoli) brown field in Southern Italy. A large integrated steelworks operated in this area. The authors conclude that, based on the geochemical information received from a large number of analyzed water and soil samples, the natural volcanic hydrothermal fluids are mixing with the anthropogenic component, complicating the remediation efforts. The real pollution to be remediated would have been the occurrence of POPs (namely, PAH and PCB), distributed in different spots across the brownfield site. Although the remediation was completed in 2009, serious questions arose concerning the remediation execution and implementation. At this writing, the case is in litigation before the Napoli Tribunal. **Iadarola *et al.*** discuss the management of hazardous by-products of urban waste incineration. Although incineration is regarded as an effective technique for solid waste management, it has some weaknesses. Flue gas contains large amounts of macro- and micropollutants and the residues are regarded as hazardous waste. The authors give examples of how this problem is solved in Italy.

Health issues are an important part of environmental geochemistry. Some essential and interesting examples are dealt with in four chapters.

Finkelman *et al.* introduce the medical geology theme by emphasizing that all macro- and micronutrients that are essential for our health and well-being come from the rocks that are at or beneath the surface of the earth. The mechanisms as to how these nutrients migrate from rocks, to soil, to our bodies and what chemical reactions they participate in our bodies, thus affecting our health for better or worse, are geochemical processes that are the heart of medical geology. **Harvey Belkin** presents the problems connected with poorly efficient and commonly unvented stoves which cause significant indoor air pollution in China. This pollution consists of mixtures of particulate matter, various gases, and complex organic compounds such as dioxins, polycyclic aromatic hydrocarbons formaldehyde, and polychlorinated dibenzofurans. The pollution affects cooks, generally women and their young children, causing various respiratory and nonrespiratory diseases. **Nadine Piatak** discusses the environmental characteristics and utilization potential of metallurgical slag, which can be an environmental liability or a valuable resource. Based on studies on the legacy steelmaking slag from the Chicago area, USA, she introduces an evaluation tool used to help categorize a particular slag as an environmental hazard or a valuable by-product. **Mark Lyles** deals with the health risk caused by dust in the Middle East desert areas. He studied the dust samples for their physical, chemical, and biological characteristics and for their potential to cause adverse health effects. The mineralized microparticulate dust was composed of a $CaCO_3$ coating over a matrix of metallic silica crystals containing a variety of trace metals constituting ~1% by weight of the PM10 particles. These particles additionally contained ~1% by weight bioavailable aluminum and reactive iron. Microbial analysis revealed a significant biodiversity of bacterial, fungi, and viruses, of which ~30% are known pathogens.

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