

DETERMINATION OF BLACK CARBON IN LACUSTRINE AND COASTAL MARINE SEDIMENTS BY THERMAL OXIDATION

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Received 06-12-2000

Abstract

A thermal oxidation method was used to determine black carbon (BC) distribution in recent lacustrine sediments in four remote alpine lakes, i.e. Lake Krisko Sup., Lake Ledvica, Lake Krn and Lake Planina, in subalpine Lake Bled and in the coastal marine sediment in the Gulf of Trieste (northern Adriatic). Additionally, total carbon, organic carbon (OC) and total sulphur were also analysed. Sedimentation rates were determined by measuring ²¹⁰Pb activity. The lowest BC/OC ratios were noted in remote mountain lakes, ranging between 5–8% and depending upon precipitation amount. In Lake Bled, the BC/OC ratio increased to 10%, but the highest BC/OC ratio was determined in the Gulf of Trieste, reaching 17%. A difference between atmospheric deposition input of BC into sediments in remote, clean areas and surface runoff and riverine input of BC in urbanised, polluted areas is clearly seen.

Introduction

Black carbon (BC) is one of the ubiquitous materials circulating around the surface of the Earth. It is found in the air, soil, sediment, water and ice. BC is a relatively inert form of carbon, comprising a range of materials from highly polyaromatic to elemental or graphitic carbon, produced by the incomplete combustion of fossil fuels and biomass.¹ But, as pointed out by E. Goldberg,² there is no unambiguous definition of BC. However, a new definition of BC was recently proposed by Kuhlbusch and Crutzen,³ based on the quantitative determination of the molar H/C ratio in the sample.

BC is a chemical and microbial inert substance.⁴ Due to its inertness, BC in soils, sediments and ice persists over long periods of time.^{5,6} BC in the atmosphere is the principal component involved in absorption of solar radiation and, thus affects the Earth's radiative heat balance.⁷ It also acts as an efficient cloud condensation nucleus, as an important carrier-phase of pollutants such as polycyclic aromatic hydrocarbons (PAHs),⁸ and as a catalyst of various reactions in the atmosphere.⁹

BC in sediments can be used as an environmental indicator. Since the beginning of the industrial revolution, BC has been emitted into the atmosphere in increased

quantities,¹⁰ and dispersed over wide areas by air currents. From the atmosphere, BC is deposited by both wet and dry deposition. Consequently, the depth profiles of BC in recent sediments can be used as an excellent tracer of fossil fuel usage and wildfire events in the past.¹¹ When determining BC distribution in sediments, the temporal and spatial impact of anthropogenic activities on the environment can be also evaluated.

Various analytical techniques based on the chemical and physical properties of BC were used in the past in order to determine BC in samples of different matrices.¹ Initially, optical instruments were used. On the basis of the colour and shape of BC particles, it is possible to distinguish them from other inorganic material or degraded plant tissues and to identify the source of BC. These microscopic techniques (e.g. Light and Scanning Electron Microscopy) can be used either qualitatively or quantitatively. On the other hand, some analytical techniques using spectroscopy were also developed. Raman and Infrared Spectroscopy and ¹³C-NMR were mainly used in the last decades. The main disadvantages of these methods are that quantitative determination is difficult and that some methods are time-consuming. In recent years, thermal treatment became the most common method to determine BC in samples of various matrices. The method is relatively fast, quantitative determination is possible but structural information and identification of the source of BC are lost. However, these analytical methods were designed and developed for specific scientific purposes. Individual BC methods rely on operational definitions of BC, and thus it is crucial to know how measurements made by different techniques relate to each other. At present, very little is known about the comparability of individual BC techniques, also because of the fact that a BC reference material is not yet established.¹²

The objective of this work was to determine the BC distribution in some alpine lacustrine and coastal marine sediments using thermal oxidation. Vertical profiles of BC dated by ²¹⁰Pb and determined in remote alpine lacustrine sediments, with almost no human influence, were compared to the vertical profiles of BC determined in subalpine lacustrine and coastal marine sediments, where a strong anthropogenic impact is present. In addition, the organic carbon (OC), total carbon (TC) and total sulphur (TS) concentrations were also measured in the sediment samples and the BC/OC ratios were

calculated. In selected samples, the shape and surface morphology of BC particles were analysed using a scanning electron microscope. EDS spectra of selected particles were also derived to obtain the qualitative elemental composition of the particles.

For the study area, four remote, high altitude mountain lakes situated in the Julian Alps were selected, i.e. Lake Krisko Sup., Lake Ledvica, Lake Krn and Lake Planina. All the lakes are of glacial origin. They are small (surface area of 0.6 to 5 ha), shallow (9.5 to 17 m) and surrounded by steep slopes. The main bedrock is limestone. The annual precipitation rate is high, reaching 3200 mm per year in the NW part of the Julian Alps and decreasing in the SE direction.¹³ There are no permanent surface inflows into these lakes. All of the lakes are situated in the Triglav National Park, where human impact is limited by law, except for Lake Planina, where there is a mountain hut, situated just above the lake.

In addition, two sites in urbanised areas were also selected, i.e. Lake Bled and the Gulf of Trieste (northern Adriatic). Lake Bled is an eutrophic subalpine lake, also of glacial origin, with a surface area of 1.5 km², a maximal depth of 30 m and with several surface inflows. Deeper layers of the water column are anoxic and in the sediment methanogenetic processes are present.¹⁴ In the Gulf of Trieste, the sampling station AA1 in the central part of the Gulf was selected, at a depth of 21 m. The Gulf of Trieste is a shallow marine basin, with several freshwater inflows. Sedimentary detrital material originates primarily from the Soča/Isonzo river which is the main freshwater inflow. The uppermost layer of the sediment is bioturbated.

Experimental

Sampling

In 1998, six sediment cores were collected from the above mentioned locations in Slovenia. All of the lacustrine sediment cores were taken from the deepest basin of each lake. Additionally, a core from the coastal marine sediment in the Gulf of Trieste (northern Adriatic) was also taken (sampling station AA1). All cores were collected using a gravity core sampler fitted with a plexiglass tube 6 cm in diameter and 70 cm long. The cores were immediately extruded in the field and sectioned into one cm thick

intervals. Subsamples were freeze dried, sieved through 100 µm mesh, homogenised and stored in polyethylene vials until analysis.

Black carbon determination

All subsamples were pre-treated in order to remove inorganic and organic carbon. First, organic carbon was removed by thermal oxidation at 375 °C for 24 h in the presence of air.¹⁵ Subsequently, inorganic carbon was removed through an acidification procedure using 1 M HCl acid. Considering that all the sampling sites are situated on limestone bedrock, violent effervescence was prevented by adding a small quantity of distilled water before acidification. Then, 1 M HCl acid was added until effervescence upon acid addition ceased, indicating complete removal of inorganic carbon. After sample pre-treatment, the BC concentration was measured using an elemental CHNS analyser (Carlo Erba Inst., EA 1008) at a combustion temperature of 1020 °C. The precision of the method, expressed in terms of the standard deviation, ranged between 5-10%.

Organic carbon, total carbon and total sulphur determination

When determining organic carbon (OC), samples were treated with 1 M HCl in order to remove inorganic carbon.¹⁶ The OC content was again determined using an elemental analyser at a combustion temperature of 1020 °C.

When determining total carbon (TC) and total sulphur (TS), the samples were analysed using an elemental analyser, without any sample pre-treatment. The precision of these measurements, expressed as the standard deviation, was 3-5%.

Scanning Electron Microscopy and X-ray Energy Dispersive Spectrometry

A JEOL JSM 5800 scanning electron microscope (SEM) was used for overall microstructural analysis and examination of the surface morphology of sediment samples. Prior to SEM analysis, the sample was mounted on carbon conducting tape to provide the sample with electrical conductivity and a charge effect. The SEM was equipped with a LINK ISIS 300 energy dispersive X-ray (EDS) analyzer. The EDS

system allows non-destructive qualitative elemental analysis of visually selected areas on the surface of the selected particle in the sediment samples.

Determination of sedimentation rates in the sediments

All sedimentation rates were determined by measurement of ^{210}Pb activity, which was determined by γ -ray spectrometry using an HP Ge well-type detector and a Canberra 90 multichannel analysis system.¹⁷

Results and discussion

Black carbon particles

The shape and surface morphology of the BC particles were analysed with SEM. Figs. 1 and 2 show BC particles from the sediment sample from Lake Bled. The spherical BC particle shown in Fig. 1 originates either from coal or oil combustion. Further decoding of its origin is possible when the EDS spectrum of the BC particle is measured, as shown in Fig. 3. Since in EDS spectra hydrogen can not be detected, the Kuhlbusch and Crutzen definition of BC,³ in terms of the H/C ratio can not be used. Instead, the O/C ratio emerged as a suitable option to define BC particles in the EDS spectra. When the O/C ratio of a selected particle is below 0.15 the particle can be considered as a BC particle, but its origin can only be predicted from the element composition.¹⁸ The O/C ratio of the particle in Fig. 1, evaluated from Fig. 3, is 0.08. Hence, it can be considered as a BC particle. Because of the presence of S in the EDS spectrum, the most probable origin of this BC particle is from coal combustion. Si and Ca were also detected in small quantities since some mineral particles are also present in the sample. A typical BC particle originating from biomass burning is presented in Fig. 2. This particle retains its original plant structure and the length to width ratio is larger than 3.

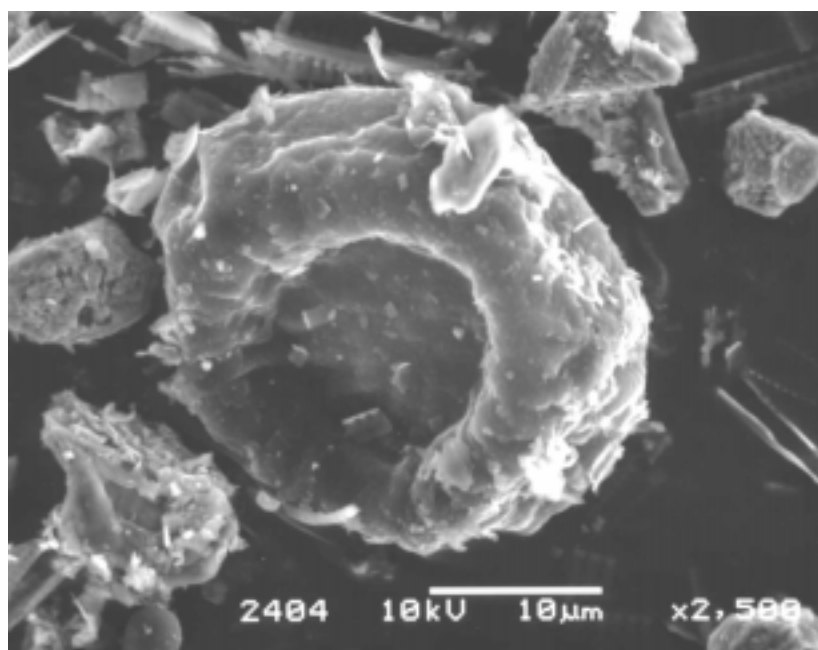


Fig. 1 : Spherical BC particle from the sediment of Lake Bled

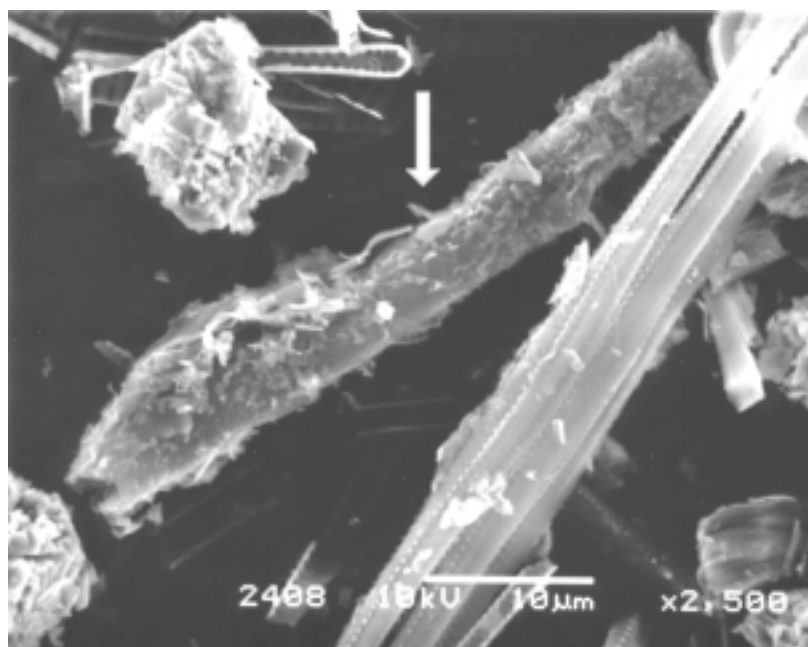


Fig. 2 : Biomass BC particle from the sediment of Lake Bled

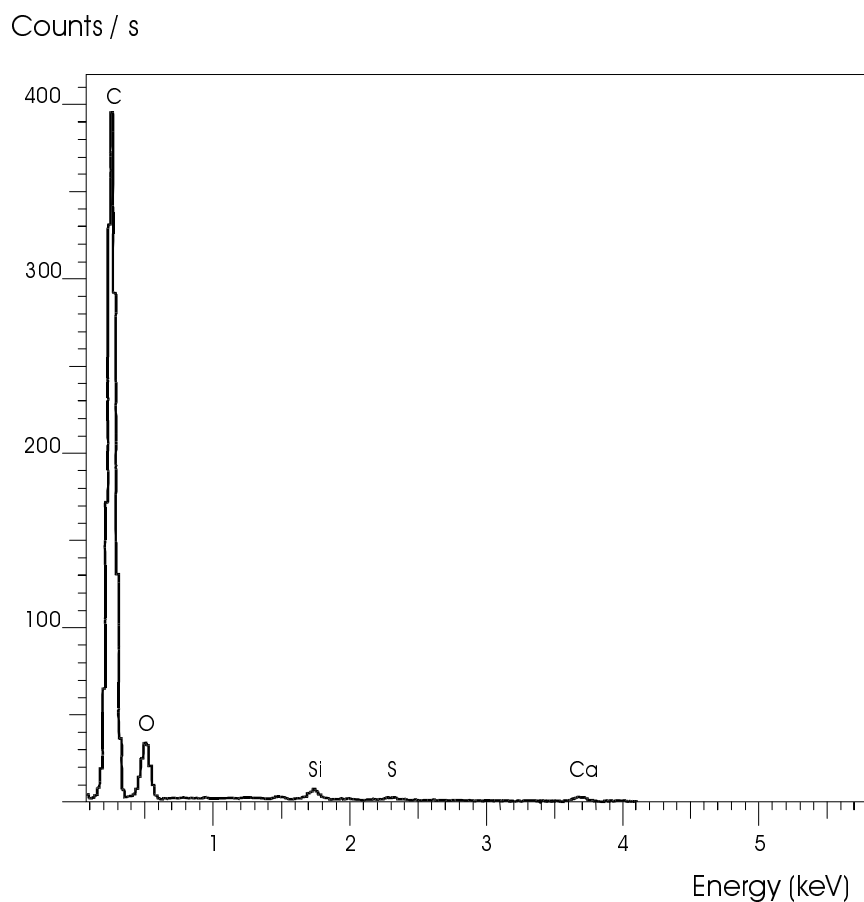


Fig. 3 : EDS spectrum of the spherical BC particle presented in Fig. 1

Black carbon content in sediments

BC contents in the studied sediments ranged from 1 to 11 mg BC/gdw (gdw = gram dry weight sediment) (Figs. 4 and 5). The highest contents were measured in the alpine lacustrine sediments, while in the urban sediment of Lake Bled and in the coastal marine sediment in the Gulf of Trieste the BC contents were much lower. The BC concentrations in Lake Bled did not exceed 5.5 mg BC/gdw. In the coastal marine sediment, the BC contents were even lower, ranging from as low as 0.5 to 1.5 mg BC/gdw. A decreasing vertical distribution of BC contents in the alpine lacustrine sediments was observed, with the exception of Lake Planina sediment, where a marked peak, dated to about the year 1950, is evident (Fig. 4). This peak is related to a huge

forest fire in the year 1948 in the vicinity of that lake, emitting large amounts of BC in the lake catchment area.

The BC distribution in the sediments of Lake Bled and the Gulf of Trieste showed a different, characteristic vertical profile. At the beginning of the 20th century, concentrations began to increase, reaching maximal values in the 1960s. These high values could be explained by increasing industrialisation and rapid increase in fuel consumption. In the 1970s concentrations of BC decreased rapidly, probably due to a shift from coal and oil to gas energy sources. The BC concentrations in the lower layers of the coastal marine sediment, averaging to about 0.5 mg BC/gdw, could be considered as the pre-industrial BC content in the sediment of the Gulf of Trieste.

Organic carbon, total carbon and total sulphur contents in sediments

The OC distribution in the sediments (Figs. 4 and 5) showed a similar pattern. Again, the highest concentrations were measured in the alpine lake sediments. The OC concentrations in these sediments ranged between 60 and 170 mg OC/gdw. The inflow of organic matter from the lake catchment area and the accumulation of organic matter in the deepest part of the lake could be the source of such high OC concentrations. The OC concentrations in Lake Bled were lower, ranging from 20 to 50 mg OC/gdw. In the Gulf of Trieste, the OC concentration was even lower, reaching a maximal value of 15 mg OC/gdw. In all sediments, vertical distributions of OC content showed a decrease, while a nearly exponential decrease of OC content was observed in the Gulf of Trieste.

The TC distribution in the sediments is also similar to that of OC. The highest values, reaching 200 mg TC/gdw, were measured in the alpine lake sediments, while the lowest values, not exceeding 60 mg TC/gdw, were again determined in the coastal marine sediment. In the lower layers of the lacustrine sediments, the TC contents approached 125 mg TC/gdw, showing that OC is mainly decomposed and only carbonates are left.

The TS distribution in the studied sediments is shown in Fig. 6. The lowest concentrations, below 3 mg TS/gdw, were measured in unpolluted, remote mountain lakes. Higher concentrations were noted in polluted and anoxic sediments from Lake

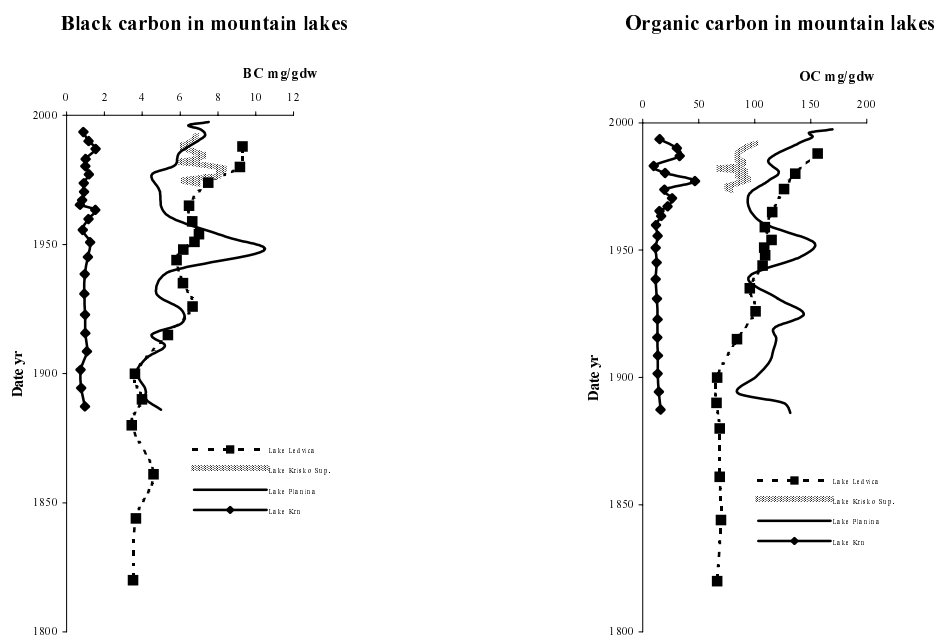


Fig. 4 : Vertical profiles of black carbon and organic carbon in mountain lakes

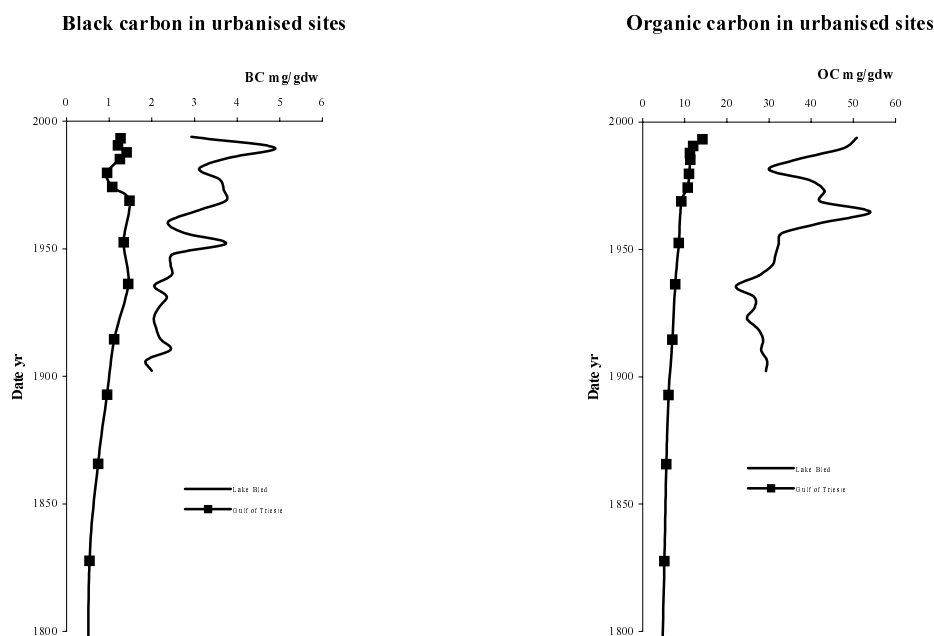


Fig. 5 : Vertical profiles of black carbon and organic carbon in urban sites

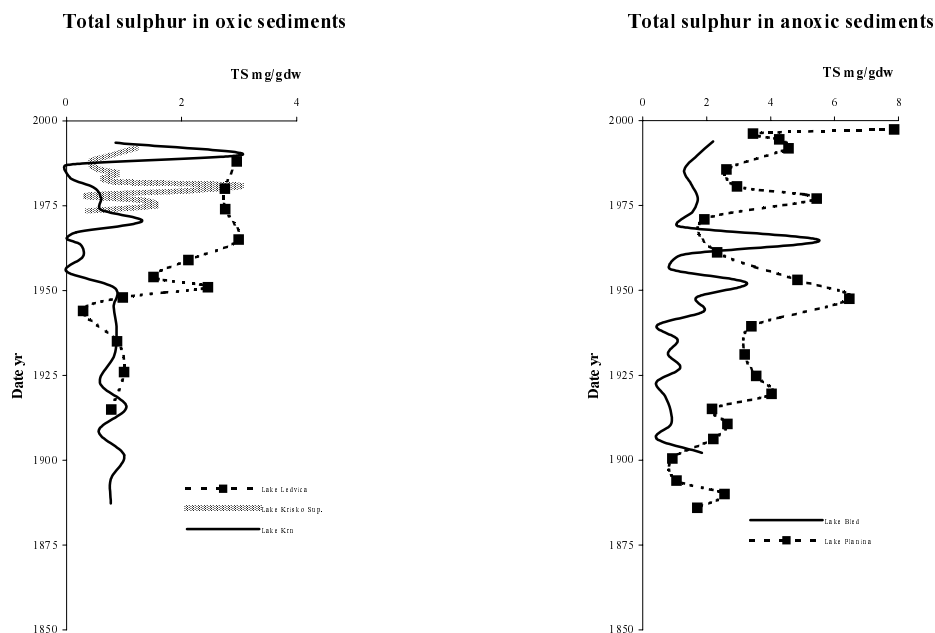


Fig. 6 : Vertical profiles of total sulphur in oxic and anoxic sediments

Planina and Lake Bled, reaching almost 7 mg TS/gdw. The main source of sulphur in these lacustrine sediments is most probably atmospheric deposition of sulphate.¹⁹ A decrease of TS concentrations in the sediments is observed. Generally, more fluctuating peaks in the upper layers of the sediments are noted and are related to variations of atmospheric deposition of the pollutants, but in the lower sediment layers, dated before 1950, the concentrations decreased rapidly indicating lower pollution impact. On the other hand, the distribution of TS in anoxic sediments is different due to sulphate reduction and pyrite formation resulting in a rapid increase of TS concentrations in the lower layers of the sediments.

The parallel depth decrease of BC and TS concentrations in the remote lacustrine sediment cores documents the common source of both pollutants, i.e. atmospheric deposition.

BC/OC ratio in sediments

The BC/OC ratio is a characteristic property of a study area and can be related to the relevant pollution phenomena. All BC/OC ratios in alpine lakes were below 10%.

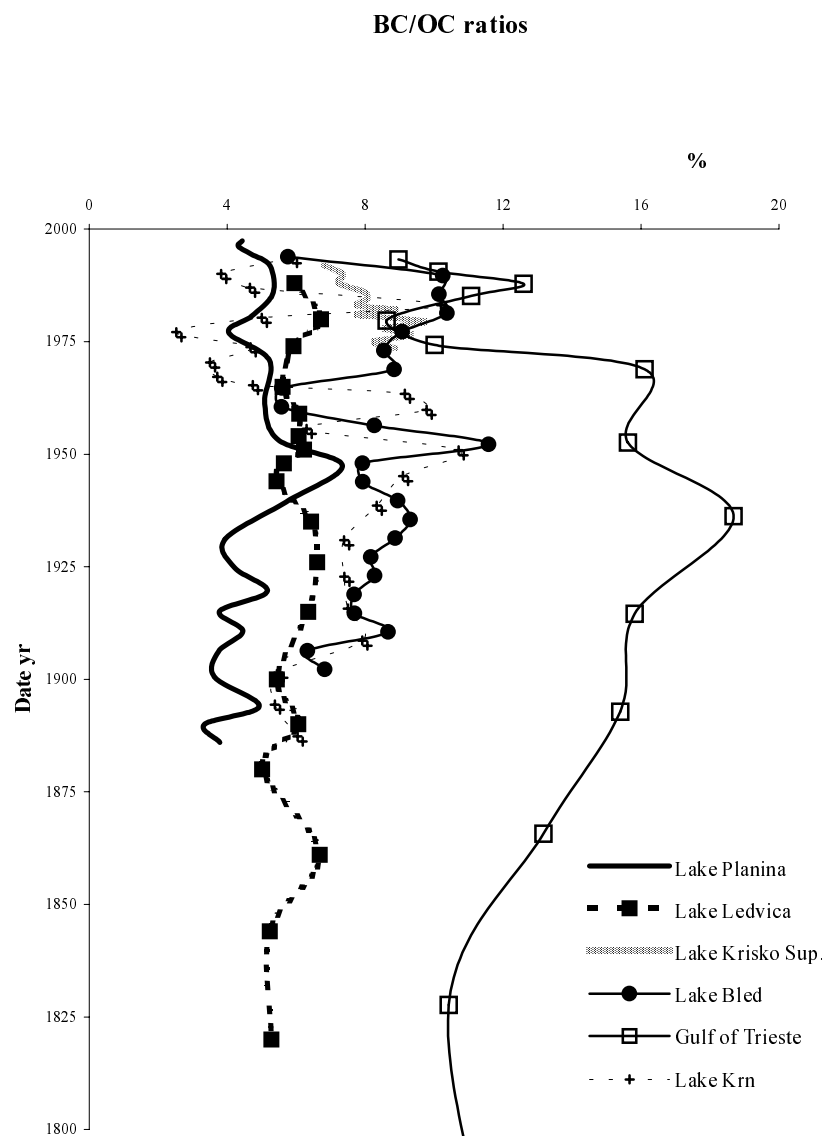


Fig. 7 : Vertical profiles of BC/OC ratios in lacustrine,²⁰ and coastal marine sediments

Higher BC/OC ratios, exceeding 10%, were measured in Lake Bled which is surrounded by an urbanised area. The highest ratios, reaching almost 20%, were encountered in the Gulf of Trieste (Fig. 7). Nearly constant vertical profiles of BC/OC ratios were found in the alpine lacustrine sediments, showing a small but constant input

of BC. An evident decrease of the BC/OC ratios in the W - E direction across the alpine area is observed due to decreasing atmospheric deposition. Atmospheric deposition is the main source of input of pollutants in remote alpine areas. The western part of the Julian Alps receives the highest quantity of precipitation, and hence pollutants, which is also reflected in a higher BC input and higher BC/OC ratios in sediments. Going further to the east, the annual precipitation rate, the BC input and the BC/OC ratios decrease. The rather uniform vertical sedimentary profiles of BC/OC ratios detected in alpine lacustrine sediments also indicate that local sources of BC pollution are less important than atmospheric deposition.

The BC/OC ratios in the sediments of Lake Bled and the Gulf of Trieste were much higher than in remote alpine lakes indicating that local sources of pollution, entering by fresh water inflows, are more important than atmospheric deposition. The increase of BC/OC ratio started at the end of 19th Century in parallel with industrial development and the increasing use of fossil fuel. The highest ratios were observed in the years after the Second World War and then decreased in the late 1970s, most probably due to improved air pollution emission control, achieved through installation of control devices, and a shift in fuel consumption from coal and oil to natural gas, resulting again in reduced emissions²¹. Similar vertical profiles of BC in recent sediments were also reported in other lacustrine and coastal marine sediments.⁶

Conclusions

The concentration of BC has been changing in the last two centuries according to the level of pollution. Hence, BC in sediments can be used as a good environmental indicator. Using the vertical profile of BC contents in recent sediments, the temporal and spatial impact of anthropogenic activities, e.g. fossil fuel usage and forest fire events, on the environment in the last 150 - 200 years can be evaluated.

The thermal oxidation method was used to determine BC contents in selected lacustrine and coastal marine sediments in Slovenia. Regarding the data, it is evident that human impact on remote mountain areas is slight. The only exception is Lake Planina

because of the mountain hut situated above the lake. The highest BC/OC ratio was determined in Lake Krisko Sup. and the lowest in Lake Planina. The BC/OC ratios decreased in the W - E direction, following the decrease in precipitation in the same direction. Therefore, the main source of BC in these sediments is atmospheric deposition, because other local sources of pollution are absent.

The study sites in Lake Bled and in the Gulf of Trieste showed a different distribution of BC. They are situated in urbanised area where a strong human influence is present. The main sources of BC in these sediments are riverine input and surface runoff. A characteristic vertical distribution of BC/OC ratios appeared, reaching maximal values in the 1960s, when pollution seemed to be the most intensive, but decreasing in the last decades of the 20th Century when emissions of pollutants were efficiently reduced.

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Povzetek

Za določitev koncentracije črnega ogljika (BC) v sedimentih štirih visokogorskih jezer (Zgornje Kriško jezero, Jezero v Ledvicah, Krnsko jezero in Jezero na Planini pri jezeru), v Blejskem jezeru in v obalnem sedimentu v Tržaškem zalivu smo uporabili termično metodo. V vzorcih sedimenta smo določili še koncentracije totalnega in organskega ogljika ter totalno žveplo. Starosti sedimentov so bile določene z merjenjem aktivnosti ^{210}Pb . Najnižje vrednosti razmerja BC/OC smo izmerili v visokogorskih jezerih. Vrednosti so nihale med 5-8%. Razmerje BC/OC v Blejskem jezeru je naraslo na 10%, medtem ko je v Tržaškem zalivu znašalo 17%. Opisane vrednosti nam pokažejo razliko med neonesnaženim visokogorjem, kjer je glavni izvor BC v sedimentu atmosferska depozicija, in med onesnaženim urbanim okoljem, kjer sta izvor BC v sedimentu vnos z rekami ter spiranje površja.