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제주도 호소퇴적물을 이용한 인위적 대기
중금속 오염사 규명

A history of the anthropogenic pollution for lead in the
East Asia as documented in peat bog sediments at
Cheju Island, Korea

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본 보고서를 “제주도 호소퇴적물을 이용한 인위적 대기중금속 오염사 규명” 과제의 최종보고서로 제출합니다.

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요 약 문

I. 제 목

제주도 호소퇴적물을 이용한 인위적 대기 중금속 오염사 규명

II. 연구목적 및 중요성

산업혁명을 거치면서 전세계적으로 비철금속의 수요와 화석연료 사용량이 급격히 증가하면서, 더불어 중금속 오염물질의 대량 방출에 따른 국지적·대규모적 대기오염을 유발하면서 심각한 환경문제를 야기하게 되었다. 특히 20세기 이후에는 자동차 산업의 급속한 성장과 이에 따른 유연휘발유 사용량의 증가는 대기내의 납 농도를 수백 배까지 증가시켰다. 이는 인류역사상 단일 오염원에 의한 가장 큰 대규모적 대기 오염을 야기하여 선진 각국에서 유연휘발유의 사용을 억제하고 무연휘발유 사용의 한 계기가 되면서 중금속에 의한 대기오염을 국제적 공동관심사로 부각시켰다. 따라서 이후에 국제적으로 대기오염의 정도와 범위를 규명하려는 연구가 활발히 진행되어 왔고 특히 과거의 오염과정을 추적함으로써 진행과정을 규명하고 앞으로의 환경오염을 억제하기 위한 연구가 각국에서 수행되고 있다. 즉 호소퇴적물, 토탄층, 그리고 해양퇴적물 등을 이용한 국지적 규모의 오염을 연구하거나 극지방의 빙하를 이용하여 지구 차원적 오염사 연구가 수행되고 있다.

우리 나라를 포함한 중국과 일본이 위치하고 있는 동북아시아 지역은

경제발전이 급속도로 진행되어온 지역의 하나로서, 타 지역과 마찬가지로 오늘날 대기오염이 심각한 수준에 이르고 있다. 하지만 아직까지 과거로부터 오염의 진행과정을 규명한 연구가 미미한 실정으로 과거의 현상을 바탕으로 오늘날의 오염 범위와 규모를 정확히 파악하기 위한 자료 획득과 기반이 마련되어 있지 못한 것이 현실이다.

이에 동북아 3개국에 의한 대기 오염사를 규명하기에 적합한 제주도 호소퇴적물을 이용하여 가장 적합한 대기오염 추적원소인 납의 농도변화를 분석함으로써 시대별로 어느 정도 오염이 진행되어 왔는가를 연구하고자 한다.

III. 연구내용 및 범위

제주도 한라산 주변 기생화산인 동수악의 분화구에 형성된 호소퇴적물을 채취하여 깊이별로 시료를 절단하여 먼저 함수율, 유기물 함량, 밀도를 각각 측정하였다. 자료 해석에 가장 중요한 퇴적률과 연대 추정은 Pb-210의 분석을 통해 이루어 졌다. 그리고 주 원소성분은 XRF를 이용하여 분석하였고 납의 농도는 ICP-MS를 이용하여 분석하였다. 또한 자연적 바탕값에 비해 상층부로 갈수록 증가하는 납성분의 농도가 인위적인 오염물질에 의한 것인지를 확인하기 위해 납안정동위원소 (Pb 204, 206, 207, 208)의 비를 분석하였다. 호소퇴적물 분석을 통해 획득된 납 농도 변화의 시간적 추이는 여러 자료를 통해 복원된 동북아시아 3개국에서 시대별 중금속 배출량 추이와 상호 비교를 통해 인위적 오염과정임을 규명하고자 하였다.

IV. 연구 결과 및 토의

국내 최초로 호소퇴적물을 이용하여 과거의 대기오염사를 복원한 결과, 제주도 지역에서 납의 대기 강하량은 19세기 중엽까지 자연적 바탕값을 유지하고 있었으나 이후 납의 강하량이 뚜렷한 증가하였음을 보인다. 특히 20세기 중반이후 급격하게 증가하여 자연 값보다 4배 이상 증가하였음이 밝혀졌으며, 이것은 납의 주 배출 오염원인 비철금속의 생산량과 화석연료 사용의 급증에 의한 것으로 해석되며, 유연휘발유의 사용에 의한 납 오염물질의 배출도 크게 기여한 것으로 보인다. 본 연구지역의 대기 오염의 주 영향 국가는 현재의 자료만으로 규명하기 어려우나 납 오염물질은 3개국 모두에서 이동되어 온 것으로 사료된다. 납안정동위원소 비의 분석을 통해 퇴적물 시료에서 나타나는 납성분의 시간적 증가 추이는 인위적 오염물질에 의한 것임이 명확히 입증되고 있다.

본 연구를 통해 동북아시아 지역에서도 세계의 다른 지역과 마찬가지로 납에 의한 대기 오염이 지난 100여 년 전부터 발생하였으며, 오늘날까지 지속적으로 증가 추세에 있음이 밝혀졌다. 이러한 결과는 현재 중국의 경제성장이 가속화되고 있고, 이에 따른 화석연료 사용의 급증으로 21세기에도 중금속에 의한 대기오염이 가속화될 우려가 있음을 나타내는 것으로 각국이 배출량 규제 등을 통한 대기 오염에 공동으로 대처하여야 할 필요성을 제시하고 있다.

SUMMARY

I. Title

A history of the anthropogenic pollution for lead in the East Asia as documented in peat bog sediments at Cheju Island, Korea.

II. Significance and Objectives of the Study

Worldwide increase in demand of non-ferrous metals and use of fossil-fuels since the Industrial Revolution induced on a regional and global scale severe environmental pollution due to heavy metals emitted into the atmosphere. In the 20th century, sharp expansion of the automobile industry followed by the use of large amounts of leaded gasoline have become a major source contributing to great increase of airborne lead. Use of lead additives in gasoline was responsible for the most widespread and intense anthropogenic pollution for lead in the atmosphere in history. This was indeed one of the reasons why the developed countries started to introduce lead-free gasoline and to become active in making the measures for the environmental protection. Since then, many investigations have been made to reconstruct temporal trends of the atmospheric pollution and to establish a baseline of natural background level in various regions. A historical atmospheric

pollution could be recorded on a regional scale in lake, peat, and marine sediments, while on a global scale in polar ice sheets.

In the East Asia including China, Korea and Japan, the industrialization and economic growth have been very rapid, which means that the atmospheric pollution is likely to become significant. Despite the present-day situation, no study has been performed to reveal time trend of the atmospheric pollution in this region, in spite of the fact that an assessment of the past atmospheric pollution is absolutely needed to understand the extent of anthropogenic perturbation of the atmospheric burden of various heavy metals.

The aim of this study is to investigate the historical atmospheric pollution for lead caused by the human activities in China, Korea, and Japan, using the peat bog sediments collected at Cheju Island, Korea.

III. Scope of the Study

The peat bog sediments sampled on a small crater, situated on Mt. Dong Su Ak, Cheju Island, Korea, were sliced into 1 cm increment. Firstly, the contents of organic material and the bulk density in sediment were firstly measured just after subsampling. The ages of the sediments were estimated by Pb-210 geochronology. Major elements were analysed by XRF and trace elements by ICP-MS. The stable lead isotopes (Pb 204, 206, 207, 208) were also determined to verify the

anthropogenic source of the excess Pb in sediments. In order to make the interpretation of data reliable, the comprehensive informations available on the amounts of production of non-ferrous metals and use of fossil-fuels in three countries during the past times were gathered and compiled in this study.

IV. Results and Discussions

From the result of this study, it is found that the atmospheric Pb flux in the region investigated did not increase until the middle 19th century in comparison with the natural background level. After slight variation of Pb concentrations until the early 20th century, however, a significant increase in concentration occurred about 45 years ago. The enrichment factors calculated by a reference element (Al) in the upper sediments are found to be higher by a factor of 4 than that of the natural level, which is likely due to anthropogenic lead emitted from non-ferrous metals production and the burning of the fossil fuels as well as combustion of leaded gasoline. While it is not evident which country was a dominant contributor to this atmospheric pollution for lead, it is probable that the Pb aerosols emitted from three countries have been transported to this investigated region. Determination of the stable lead isotopes supports the fact that the excess Pb in sediments is anthropogenic in origin.

This investigation revealed conclusively that the atmospheric pollution for lead became significant about 100 years ago in the East Asia and has remained increasing trend in atmospheric Pb flux until the present. In addition, the results imply that the atmospheric pollution for lead could be severe in the future, because of the vast demand of fossil fuels like coal in China. Therefore it is necessary to come to an international agreement with reducing the emission of heavy metals to the atmosphere.

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1. INTRODUCTION

The global and regional record of changes in the atmospheric deposition of various elements released by human activities such as pollutant sulphate and heavy metals has been shown to exist in the different environmental repositories such as coastal ocean areas (Chow, 1973), lake and pond sediments (Nriagu and Coker, 1983; Thomas et al., 1984; Verta et al., 1989; Renberg et al., 1994), polar snow and ice (Murozumi et al., 1969; Boutron et al., 1991; Hong et al., 1994, 1996) and peat bogs (Schell, 1986; Markert and Thornton, 1990; Shotyk, 1996). These studies demonstrated that the atmospheric pollution for trace elements has affected a regional and even global biogeochemical cycling and the increased deposition of these elements has resulted in severe environmental contamination in the world. With increasing population and industrialization, emissions of toxic trace elements would increase continuously to result in direct and indirect effects on human health. In fact, environmental contamination by human activities has already become serious in the world since the beginning of this century (Nriagu, 1990).

The East Asia is one of the regions where the economic growth and industrialization are very rapid. Therefore we can imagine that the anthropogenic emissions of various elements from fossil fuel combustion and industrial activities may be large. From several investigations, it is

well known that the loading of sulfate and trace metals in the atmosphere of East Asia is indeed significantly elevated due to human activities (Uematsu et al., 1992; Akimoto and Narita, 1994; Mukai et al., 1994). In order to accurately assess the present day impact of atmospheric emissions of these pollutants on the environmental compartments, however, it is needed to reconstruct the past change in the atmospheric deposition fluxes and to quantify the relative importance of natural versus anthropogenic emissions of trace elements to the atmosphere. These attempts can be possibly made by investigating the historical record documented in the environmental archives such as lake sediments, glaciers and peat bogs as mentioned above.

The aim of this study is to reconstruct the temporal trend of changing atmospheric deposition of lead, a good tracer of anthropogenic pollution, and to establish the impact of human activities on the atmospheric environment in the East Asia.

2. MATERIALS AND METHODS

2.1 Description of the Cheju site

Cheju Island is a volcanic island which is located in the East China Sea, about 100 km south of the Korea mainland, about 250 km west of Kyushu, Japan, and about 500 km east-northeast of Shanghai, China

(Fig. 1). Because Cheju Island is far from the main industrial regions in Korea, China, and Japan and is considered to be a rather clean compartment without strong local sources of industrial activities, this island is a suitable area to investigate an anthropogenic influence on the atmospheric composition in the East Asia.

Meteorological characteristics at Cheju Island are well presented in Table 1, as summarized by Carmichael et al. (1996). From the dominant wind direction with season, it is found that Cheju Island could be influenced by the different air masses passing over the surrounding countries with a high seasonality. In winter, the air masses moving from the north reach Cheju Island, which results in an influence of anthropogenic emissions from North and South Korea. In spring, the air masses from the northern half of China are dominant, indicating a strong influence of the substances emitted from this region including Asian dust. In summer, the prevailing winds are from the south-southeast, representing an influence of southern China, Pacific maritime conditions, and southern Japan. Finally in the fall, the air masses come from the east-northeast with the predominant loading of anthropogenic aerosols emitted from Japan and Korea. The precipitation is much greater during the summer in a whole year. When considering the above mentioned seasonality of the wind pattern, it is evident that the atmosphere at Cheju Island is subject to an influence of the anthropogenic pollutants emitted from the surrounding countries.

2.2 Sampling site and sample acquisition

Cheju Island has a main volcanic peak (elevation about 2000m above sea level) and many parasite volcanoes. The sampling was made on a small parasite volcano (Mt. Tong Su Ak, 33 ° 21'15.6"N, 126 ° 37'32.4"E, elevation 675m a.s.l.). Well developed flat peatland (organic sediments) is found near the peak of this mountain. Type of this peatland is ombrogenous, i.e. peat bog developed where all precipitation is from the atmosphere (Damman and French, 1987). Therefore nutrient and trace material input must come from the atmosphere and not from runoff or from springs in the watershed. There has been little influence of mechanical erosion of local outcrops as bulk sediment origin. This could allow us to monitor the changing flux of atmospheric chemicals of interest.

When the precipitation occurs, the sampling site is waterlogged like pond. After precipitation, however, water accumulated in this area is disappeared by the processes of evapotranspiration and downward percolation. During the dry season, grasses and mosses grow on the surface of peatland. Peat sediments were collected using an acid-cleaned acryl slabs in a pit during the dry season of spring(May 1997). That is, custom-made acryl slab (31cm×11cm×5cm) was vertically pushed to the wall of a pit. Total depth of the sediments so sampled is 120 cm long. Immediately after sample collection, the slabs were sealed and

transported to the laboratory.

2.3 Sample preparation

In the laboratory, the sediments were carefully sectioned with an acid-cleaned stainless steel spatula into 1cm increments, stored in plastic bags, weighed and freeze-dried. Care was taken to handle the slabs with clean plastic gloves and sheets. For each cutting of the sediments, 0.5 cm thick surface was chiseled away from the sides and top of the sample layer to discard possible contaminants introduced from the walls of the slab, even if the slabs were acid-washed before the sampling. The dried samples were ground in an argate mortar for homogenizing. To minimize a possible contamination incurred from suspended dusts in the laboratory, all the procedures for sample preparation were performed in a Class 100 laminar flow clean bench. In addition, all the containers which were directly contacted to the samples were rigorously acid-cleaned with Merck suprapur HNO³.

2.4 Analytical procedures

We performed all the chemical analyses of the sediments only until the depth of 60 cm to investigate the recent change of atmospheric metals deposition. On the whole increments, the content of organic

matter (loss on ignition) was determined by ashing a subsample of the freeze dried sediments at 550°C for 2 hr after drying a subsample at 105°C overnight. The bulk density of sediments with depth was also measured just after subsampling by Pycnometer (AccuPyc 1330).

Major elements, Al, Fe, Mn, Ti were analysed in each increment of sediments using X-ray fluorescence spectrometry (Philips Model PW 1480).

Trace elements, Pb, Cu, Zn, Cd, Sn, Mo, Cr were determined after total digestion of samples on the whole increments between surface to 30.5 cm and in increments of 2 or 3 cm depth intervals below the depth of 30.5 cm. The chemical procedure for determining the total content of trace elements in sediments consists in a digestion of 0.1 g dried ground sediments with HNO_3 -HF- HClO_4 (4:4:1 by volume) mixture in TFM high pressure bombs by using Microwave Digestion System (Milestone Model MLS 1200 MEGA). The dissolution was carried out by steps as follows; 5 mL of mixed acids was added to six pressure bombs containing about 0.1 g sediments and then the digestion was made by microwave oven with a program of 250 W for 5 min., 400 W for 5 min., 500 W for 10 min., and 600 W for 10 min. The solution was dried and then 2 mL of HNO_3 was added to evaporate the residue of HF. This solution was again dried and the residue was diluted in 50 mL of 1 % HNO_3 . All the digestions were carried out with Merck suprapur acids. The measurement of trace elements were performed by ICP-MS (VG

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Elemental/PQ II Plus Model). The quality control of the measurements has been checked by the blanks and standard reference material of NIST (SRM 1646, estuarine sediments). The total blank contributions from the whole analytical procedures were found to be negligible for each metal.

The contents of total carbon (TC), total nitrogen (TN), and total sulphur (TS) in sediments were determined by CNS analyzer (NA 1500 Carlo ERBA Model) standardized against BCSS-1 (marine sediments) of National Research Council (NRC), Canada.

About 100 mg of samples of dried sediment was used for the determination of lead isotopic compositions in selected samples. Each sample was digested with 5 mL of HF-HNO₃-HClO₄ (4:1:1 by volume) mixture in a Teflon beaker heated for 12 hr at 150°C by a hot plate. The cover was removed and the acids were evaporated. The residue was taken to dryness again with 2 mL of 6 N HCl and then redissolved in 1 mL of 1 N HBr. The Pb separation was performed by ion exchange (Merck AG1-X8, chloride form, 100-200 mesh) with a small Teflon column (fixation in HBr 1 N and elution with HCl 6 N). Lead isotope ratios of the resultant solutions were measured by the usual single Re filament method with thermal ionization mass spectrometer (TIMS, VG Sector 54-30) of Korea Basic Science Institute. Mass spectrometer data (corrected for mass fractionation determined by replicated measurements of standard NBS SRM981 and blank) were

usually accurate to $\pm 1\%$. All the chemical procedures were carried out in a Class 100 laminar flow clean bench inside a clean room. Pb contamination introduced during sample dissolution and leaching of sediments and chemical lead separation is of the order of less than 1 ng.

Sediments were analysed for ^{210}Pb content, by measurement of ^{210}Po (half life: 138.4 days), following the method developed by Häsänen (1977). The measurement of ^{210}Pb was made at the Laboratoire de Glaciologie et Géophysique de l'Environnement, France.

3. RESULTS AND DISCUSSION

Here we discuss on the variation of only Pb deposition in sediments, because lead is the best tracer of anthropogenic pollution resulting from the industrial activities in history and, moreover, its sedimentary records have been well interpreted by various authors as mentioned in the next sections. All the chemical compositions measured in sediments are presented in Table 2.

3.1 Age dating of the sediments

The historical monitoring of the atmospheric heavy metals fluxes depends upon obtaining sediment accumulation rates and thus on

geochronological determination of the investigated sediment layers. ^{210}Pb with correlation in the fallout pattern since the 1950s of sporadic sources such as artificial radionuclides (^{137}Cs , ^{239}Pu , ^{240}Pu) originating from nuclear weapon tests and their distribution in deposition intervals dated ^{210}Pb geochronology is in many cases necessary to establish that no systematic disturbance of the sediment has occurred. Because we have no data on the artificial radionuclides, an estimate of age dating is made by the content of ^{210}Pb only.

^{210}Pb (half-life of 22.26 yr) is a naturally occurring radioisotope in the ^{238}U decay series : $^{238}\text{U} \rightarrow ^{226}\text{Ra} \rightarrow ^{222}\text{Rn} \rightarrow ^{210}\text{Pb} \rightarrow ^{206}\text{Pb}$

^{210}Pb content is primarily the result of the decay of its gaseous parent ^{222}Rn which is produced by decay from ^{226}Ra and escapes from soils by diffusion into the atmosphere; here the ^{222}Rn decays (half-life of 3.82 days) to ^{210}Pb . The two main sources of ^{210}Pb would be atmospheric fallout scavenged by wet and dry deposition and the in situ formation from ^{222}Rn . The ^{210}Pb in excess of the amount in equilibrium with in situ ^{226}Ra ("unsupported" ^{210}Pb) is used to date the deposited sediment layers. It is assumed that ^{210}Pb is in constant flux and that it is immobilized in the sediments.

From the ^{210}Pb measured from our samples, it is found that ^{210}Pb contents tend to exponentially decrease below the depth of 4.5-5.5 cm with rather irregularly high content (depth of 5.5-6.5 cm) (Fig. 2). The mixing layer is surely present in upper 4.5 cm as indicated by the ^{210}Pb

contents. This mixing layer may result from the agitation during the storms passing over Cheju Island and/or the growth of grasses and mosses. From the data available, we cannot understand the reason why high ^{210}Pb contents is present in deeper layers. It is assumed that downward migration of surface sediments would have occurred due to the cracks originating from any severe dry season and/or due to the roots of grasses grown on the surface of peatland. Despite that an accurate estimate of sedimentation rate is difficult to be obtained, the plot of Fig. 2 including data points of high ^{210}Pb contents indicates that the sedimentation rate is approximately 2.2 mm/yr. Surprisingly, this sedimentation rate is found to be quite reasonable, as discussed from the historical trend of Pb emission rate and Pb deposition in sediments in the next section 3.5. It should be emphasized that the mixing layers (4.5 cm) in the uppermost surface of the sediments correspond to the deposition of 20 years and thus a depth-age relation calculated by a sedimentation rate of 2.2 mm/yr must be updated, using the mixed age interval (20 years). In addition, the decomposition of organic materials and the compaction of the sediments with depth can make an error in estimating an age of the sediments by a sedimentation rate. To prevent a possible error in depth-age profile, the annual deposition flux of inorganic materials (ash content) is used to estimate an age of the sediments in deeper layers, as explained in the next section.

3.2 Bulk density and ash contents

The changes in bulk density with depth are shown in Fig. 3. The bulk density between 0 and about 20 cm in sediments is stable (~ 1.15 g/cc), indicating an extended period of steady sediment accumulation. An increase of the bulk density started from the depth of about 20 cm and a peak is shown at the depth of 26 cm. Then, the bulk density is found to decrease to the depth of 44 cm and to again increase. The depth profile of the ash contents in sediments shows a trend similar with the bulk density (Fig. 4). The ash content between 0 to 20 cm is $\sim 40\%$ and increase to the deeper layers except for the depth of 44 cm or so. The ash contents are high in the deeper parts, indicating a continuous decomposition of organic material. Below approximately 30 cm, slow or negligible decomposition is shown. A peak of ash content at the depth of 44 cm may represent a sporadic period of high accumulation of organic materials due to the vast growth of grasses and mosses and/or of low sedimentation of crustal dusts. Since the highly organic surface layers are decomposed with depth, the time layers are compressed. Therefore the compaction of the layers must be corrected for ^{210}Pb age dating. Here we corrected the depth-time profile, considering that the annual deposition of inorganic materials (ash content) would remain constant. At the depth of 44 cm and so, the error range of age dating may bigger because of a slightly different accumulation event as

discussed before.

The Al and Ti profiles are similar with the distribution of ash contents (Fig. 5). The peaks in Al and Ti concentrations correspond with the peaks in ash content at the same depths.

3.3 Sedimentary record of Pb concentration

The depth profile of Pb concentrations measured is shown in Fig. 6. It is found that Pb concentrations in sediments are relatively stable (mean value of 14 ppm) below the depth of 34.5–35.5 cm. From 29.5–30.5 to 22.5–23.5 cm depth interval, Pb concentrations come to be slightly elevated (up to 18.4 ppm) and then decrease to 11.7 ppm at the depth of 21.5–22.5 cm. And then the concentration values are shown to increase steadily until the depth of 13.5–14.5 cm. The sharp increase in Pb deposition begun about 45 years ago (depth interval of 13.5 to 11.5 cm). The concentration values in sediments from 12 cm up to surface layer amount to be about 30 ppm (two times higher than in deeper layers). Considering the profiles of ash content, Al and Ti contents which increase with depth, the upward increase in Pb concentrations is striking. The temporal trend of Pb concentrations measured in peat bog sediments of Cheju Island indicates an increasing atmospheric Pb deposition in the East Asia during the recent times.

Because of the change of bulk density with depth, the concentration

values measured in each increment of the sediments do not reflect an actual variation of atmospheric Pb deposition during the period studied. Therefore normalization of Pb concentrations using a reference element is necessary to discriminate the excess amount of Pb deposited above the preindustrial natural background level which could be detected in deeper layers.

3.4 Calculating enrichment factors and changing anthropogenic Pb input with time

The variation in bulk density and ash content could be expected to have a profound effect on Pb concentrations in the sediment profile. To correct natural variations in trace element concentrations could be normalized to the ash content of the sediments. While this may be a useful approach in calculating metal enrichment, this may significantly underestimate trace metal enrichments in surface layers of peat bogs where nutrient metals such K, Mg, and Ca are concentrated by plants and contribute significantly to the ash fraction (Shotyk et al., 1992). A more widely used approach to calculate enrichment factors in peats or other environmental samples is to normalize the measured metal to crustal elements such as Al, Ti and Sc to the corresponding metal to crustal element ratio in bulk rock and soils. Al concentrations are in general used as a reference element. However, the Al solubility from

oxides, hydroxides, and silicates could be enhanced in the surface and pore waters in acidic and organic-rich bogs (Faure, 1991). In contrast to Al, the oxides of Ti exhibit extremely low solubility (Baes and Mesmer, 1976) and are highly resistant to chemical weathering. Since Al concentrations are higher than Ti in our sediments, we used Al as a reference element to minimize a possible deviation in calculation caused by the analytical errors. In fact, it is found that the concentrations of Al and Ti are highly correlated (Fig. 7).

Fig. 8 shows the enrichment factors (EFs) over time for lead in excess of its natural abundances using Al as a reference element (enrichment factors are calculated by dividing the Pb concentration values by the Al concentration in the corresponding layers). Below the depth of 35 cm, the EFs are shown to be considerably constant (mean EF of 1.4), indicating that the atmospheric Pb deposition of detrital mineral in origin did not vary with time. The EFs begin to increase from a depth of 30 cm and show a sharp increase (from 2 to more than 5) between about 20 to 10 cm in depth. From 10 cm to surface in sediments, the EFs remain high values (>5). Although the depth profile of the EFs are in good agreement with that of Pb concentrations, it is markedly revealed that an increase of atmospheric Pb deposition at Cheju Island is much higher during the period studied, being different from the aspect observed from an increase of Pb concentrations in sediments. Background level of the EF allows calculation of "excess Pb"

in the depth profile. As demonstrated in Fig. 8, from 1880 to 1917 the excess Pb was not comparable to natural Pb deposition. After 1920, the excess Pb increased steadily and began to exceed the natural Pb deposition in the early 1950s. During the following decade (1954-1963), atmospheric deposition of the excess Pb rapidly increased by a factor of about 4 above the natural Pb flux. The prominent increase of Pb content from the deeper layers to surface has been well documented in peat bogs and lake sediments at various sites (see, for example, Shirahata et al., 1980; Nriagu et al., 1982; Shotyk, 1996), interpreted as a result of increased deposition of Pb from the atmosphere. However, we cannot exclude a possibility that processes of diagenesis within sediments may also affect the vertical distribution of Pb (e.g. Carignan and Tessier, 1985).

While the remarkable ability of peatlands to preserve various metals deposited from the atmosphere is widely recognized, there is considerable uncertainty regarding the reliability of peat bog records of temporal change in metal deposition. The migration of Pb in peat profiles depends very much on the chemistry and hydrology of the peatland, neither of which are well understood. For especially Pb, however, there are many studies on consistent Pb immobility in sediments so that the record of Pb deposition in sediments can be used to reconstruct the historical atmospheric pollution (see, for example, Norton, 1986; Johansson, 1989; Schell et al., 1989; Markert and Thornton,

1990; Shotyk, 1996). Norton et al. (1990) showed good agreement between the record of atmospheric deposition of Pb recorded in peat bogs versus nearby lake sediments. Renberg and colleagues (Renberg et al., 1994) also showed that the historical record of atmospheric Pb deposition recorded in Swedish lake sediments compares very well with known records over the past 3,000 years.

Another possibility that must be regarded in the interpretation of sediment data is that metals might upwards within the sediments and bring about an enrichment in the top sediment layers by natural causes. It is known that the solubility and mobility of Fe and Mn in sediments are strongly dependent on the redox conditions (Livett, 1988; Johansson, 1989). That is, the transport of Fe and Mn occurs from the lower zones (reducing conditions) to the upper zones (oxidizing conditions), having a surface or subsurface peak of the distribution of Fe and Mn in concentration. Accordingly, surface or subsurface enrichments of Fe and Mn oxides in sediments are often associated with peaks in concentrations of lead (Ochsenbein et al., 1983). As shown in Fig. 9, however, the depth profiles of Fe and Mn concentrations are highly correlated to Al (crustal-derived) (Fig. 5), indicating no migration upwards in sediments.

As a result, it is likely that the depth profile of Pb contents observed in our peatland sediments mirrors the historical trend of increased atmospheric Pb deposition and the excess Pb above natural background

level resulted from the anthropogenic Pb emitted from the human activities in China, Korea and Japan around Cheju Island. In order to evaluate the impact of anthropogenic Pb on peatlands, a comprehensive reconstruction of Pb emission rate with time is made in the next section.

3.5 Reconstruction of the historical Pb emissions from various anthropogenic sources

There are many sources by which lead can enter the air as a result of man's activities (Nriagu, 1979; Nriagu and Pacyna, 1988). These include: from mining, smelting and refining of lead and non-ferrous metals such as copper and zinc, in which lead is present as an impurity; from fabrication and chemical operations; from weathering, burning and sanding of paints and primers; from refuse incineration; from fossil fuels combustion such as coal and oil; from steel and iron manufacture; from combustion of leaded gasoline, which is the largest source of airborne Pb during the past decades. Up to the early part of the present century, smelting and refining of lead and the other non-ferrous metals were a major source of lead released to the atmosphere. Thereafter, fossil fuel (coal and oil) combustion became a major contributor to airborne lead. During the history, the greatest single contribution of lead in the atmosphere must be the combustion of leaded gasoline in internal

combustion engines. Because of its significance, we here mention the brief history of lead additives in gasoline from the discovery of the antiknock properties of tetraethyllead in 1921 to widespread use of leaded gasoline in the world (Nriagu, 1990).

Thomas Midgley and his colleagues discovered the antiknock properties of organolead compounds at the General Motors Research Laboratory on the morning of 9 December 1921. This revolutionized the automobile industry and accompanied a sharp increase of use of gasoline with lead additives in the world until the early 1970s (Fig. 10). Of lead additives used in the world, a large fraction had been consumed in the United States as shown in Fig. 10. The consumption of lead in gasoline peaked at over 380,000 metric tonnes in the early 1970s, of which the United States accounts for about 65 % (Fig. 10). Owing to the introduction of catalytic converters and a better understanding of the risks of lead exposure as revealed by close relationship of lead in gasoline to blood lead levels (Thomas, 1995), leaded gasoline was phased out in the United States beginning in the 1970s. Although the quantity of alkyllead consumed in the United States has declined sharply since 1975, the reduction rate in the rest of the Western World has not been drastic and the use of lead additives has gone up sharply in some developing countries. Overall, however, the pressure continues to grow to remove lead additives from motor fuels in the world.

The anthropogenic sources contributing to lead emission to the air in

the East Asia including China, Korea and Japan are expected not to be quite different from those mentioned above. The historical trend of quantities of anthropogenic Pb emitted to the atmosphere is difficult to be estimated, because it is not possible to make emission factors generalized with time and region. Therefore, it should be emphasized that in this report an estimate of quantity of lead emitted to the air in three countries must be made with some uncertainty. In addition, all of the possible sources, which release airborne lead, are not treated to calculate the inventory of Pb emission in this study, because comprehensive and accurate calculation is beyond the scope of this study. Estimate of Pb emission in history was based on the fact that coal combustion, smelting of non-ferrous metals such as lead, copper and zinc, and leaded gasoline consumption consist of most of the fractions of lead release to the atmosphere on a global scale (Nriagu, 1988). To put together into total emission rate, each source is treated as described below. A comprehensive review of references available was made to reconstruct the historical production rates. References used are as follows: for the non-ferrous metals production, Statistical Summary of the Mineral Industry (1913-1970) and World Mineral Statistics (1970-1990); for coal consumption, Yearbook of Energy Statistics (Korea), One hundred years of Japan (1991), Statistical Yearbook of China (1987) and Summary of mining industry in Korea (1989); for gasoline consumption, Yearbook of Energy Statistics (Korea), Refining

Statistics Source Book (1994) and Yearbook of Petroleum (Japan).

3.5.1 Pb production

The historical trend of lead production is widely available from the early of this century. As shown in Fig. 11, Pb production rate in three countries in 1910 was low to amount to only ~3000 metric tonnes per year and then continue to steadily increase until the middle 1940s (~30000 tonnes). From the middle to the late 1940s the production rate decreased to <10000 metric tonnes. After that time a rapid increase of production rate is shown in Fig. 11. Total production of lead was about 800,000 metric tonnes in 1990, indicating more than 250 fold increase of production rate from 1910 to 1990.

Pb production curve does not directly represent a time trend of Pb emission. In order to calculate emission rate of airborne lead from Pb production, it is necessary to use emission factors that have been changed with time. Smelting procedures of lead from raw ores were indeed wasteful in the past, resulting from higher emission factor in comparison with the present one. Development of technological processes employed in the non-ferrous metal production and emission control techniques has evidently induced continuous decrease of emission factors from the past up to the present. It is very difficult to obtain detailed information on emissions of heavy metals from non-ferrous metal

smelters during the period investigated. Moreover, most information available on emission factors comes from the western countries (Pacyna, 1986; Nriagu and Pacyna, 1988). Assuming that emission factors between the East Asia and the western countries are not greatly different, we here used emission factors adopted for the calculation of emission rates in Europe. Pb emission factors (in g Pb emitted/t Pb produced) for Pb production are 9000 from the 1950s before the middle 1970s and 3000 in the 1980s, respectively (Pacyna, 1991). The emission factor before the 1950s is assumed to be two times higher than that in the period from the 1950s to the middle 1970s. To avoid abrupt decrease of Pb amount emitted due to the use of emission factors for the long period, emission factors of 6000 and 4500 were adopted to estimate emission rate for the period of the late 1970s and the early 1980s, respectively. This is likely to be reasonable, in view of the fact that technological processes and facilities of smelting Pb have been developed steadily. Here it must be noted that estimate of airborne Pb emitted in three countries may be more or less uncertain for the past decades, because in Japan which is one of the developed countries in the world, emission control equipments for the environmental protection were introduced earlier than in Korea and especially in China. Therefore, Pb emission rate presented in Table 3 is likely to be overestimated for Japan and underestimated for China and Korea. Despite uncertainty in estimate, the whole temporal trend is assumed to appropriately represent

historical Pb emissions in the East Asia. Total amount of Pb emitted to the atmosphere calculated by using the emission factors was low (<100 metric tonnes) until the middle 1920s. Pb emission was peaked in the middle 1970s (~3500 metric tonnes). After that time emission rates were slightly decreased, but maintained at a level of ~2500 metric tonnes.

3.5.2 Cu production

In the East Asia, copper is one of the most widely used non-ferrous metals. Production rate was at a level of 60000 metric tonnes per year at the beginning of this century (Fig. 12). During the period of the middle 1940s to the early 1950s, copper amounts produced decreased to ~2000-4000 metric tonnes. From the middle 1950s to the 1990s copper production has exponentially increased to amount to about 1.8 million metric tonnes in 1990. Production rate increased by a factor of 300 during this century. Among three countries, Japan is found to have been a major producer until the present day as shown in Fig. 12.

In calculation of Pb quantities emitted into the atmosphere, emission factors used for the different ages are as follows; 12,000 before the 1950s, 6000 for the 1950s to the middle 1970s, 3000 for the late 1970s, 2700 for the early 1980s, and 2000 for the middle 1980s to the late 1980s, respectively. Emission rates so estimated was ~800 metric tonnes

in 1910 and increased to ~3500 metric tonnes in 1990. It is found that from the early to the late 20th century Pb emission rate released from Cu production increased only by a factor of about 4, while increase factor of emission amount reaches to about 25 for Pb emitted from Pb production.

3.5.3 Zn production

Zn produced in three countries amounted to about 5000 metric tonnes only in 1910 and continuously increased to have reached to about 2 million metric tonnes in 1990 (Fig. 13). From the early 1970s to the early 1980s production rates are found to have maintained stagnant (~1 million metric tonnes). In the 1980s Zn production in Japan decreased slightly, but increased sharply in China and Korea. Thus, Zn produced in China and Korea led to an increasing trend of total production from the 1980s forward.

Pb emission from Zn production was low at a level of <50 metric tonnes per year in 1910 and reached to the first peak (~5000 metric tonnes) in the late 1960s and to the second peak (~3700 metric tonnes) in 1990. As like Pb aerosols emitted from Pb and Cu production, Pb emitted from Zn production did not increase continuously from the early this century up to the present.

3.5.4 Coal consumption

The historical trend of coal consumption is well illustrated in Fig. 14. The annual amount of coal consumption in three countries was ~15.5 million metric tonnes in 1900 and reached to be ~107 million tonnes. The sharp increase of consumption rate occurred 40 years ago. In 1990, coal consumption amounted to be 1,000 million metric tonnes. It is well known that at present large quantities of coal consumption in the East Asia are emitting the atmospheric sulphur pollutants which result in the environmental contamination (Akimoto and Narita, 1994).

The emission rates of Pb from coal combustion varied from 330 to 1645 metric tonnes for the period of 1910 to 1955 (Table 3). With increasing coal consumption, the amount of Pb emission come to be more than 9000 metric tonnes in 1990. Emission factors (g of Pb emitted/tonne of coal burned) used for calculating the quantities of Pb emitted are 11.7 for 1950s, 10.4 for 1960s, 8.4 for 1970 and 7.7 for 1980s, respectively (Pacyna, 1991). For China, the amount of Pb emitted from coal consumption is comparable to that from non-ferrous metals production on the whole period investigated (Table 3).

3.5.5 Pb emission from the use of leaded gasoline

Pb emission from the use of leaded gasoline is presented in Fig. 15

and Table 3. During the peak of Pb emission in 1970, the amount of Pb emitted from gasoline additives was 6150 metric tonnes. In the case of Japan, this amount is comparable to that from non-ferrous metal production. After the introduction of unleaded gasoline in Japan in the early 1970s, the emission rate of Pb show a rapid decrease, which is completely different aspect with the historical trends of Pb emissions from previously described sources.

3.5.6 Comparison of temporal changes between Pb deposition in sediments and Pb emissions from various anthropogenic sources

Surprisingly, the change of the atmospheric Pb deposition observed in our sediments is in good agreement with a historical Pb emission rate released from China, Korea and Japan (Fig. 8 and 16). The sharp increase of Pb concentrations and enrichment factors in sediments is coincident with the period of similar increase of Pb emission (from the middle 1950s to early 1960s) (Fig. 8 and 16). This supports the interpretation that the excess Pb above the natural background level present in deeper layers of the sediments was attributed to the increased deposition of anthropogenic Pb pollutants transported to the study area. Some discrepancies between sedimentary record and Pb emission rate are shown for the period of the 1940s (depression of Pb emission) and for the late 1960 (marked peak of emission rate). These

differences may have resulted from the movement of dominant air masses transporting Pb pollutants which were released from China, Korea and Japan. As shown in Table 3, the amount of anthropogenic Pb emitted from Japan was much larger than those from China and Korea until the late of the 1970s. It is, therefore, found that the Pb emissions from Japan dominated a historical trend of total Pb emission in the East Asia during this period (Fig. 16). If sedimentary record reflects a substantial temporal change of the atmospheric Pb deposition in the region studied, it is likely that the transport of Pb aerosols emitted from Japan may not have been a dominant source of the excess Pb preserved in sediments of Cheju Island. It is not indeed possible to assess to what extent Pb emitted from each country has influenced the changing deposition of the atmospheric Pb at Cheju Island. In any case, the whole similarity between the profiles of the excess Pb in sediments and Pb emission rates indicates that the atmosphere in the East Asia have been polluted for lead since the late of the 19th century, due to anthropogenic Pb emitted from China, Korea and Japan.

3.6 Pb stable isotopic signature

Lead has four stable isotopes, ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb , the latter three being formed continuously by radioactive decay in the ^{238}U , ^{235}U and ^{232}Th decay series, respectively. The abundance of these isotopes in

minerals and ores is determined by the original uranium : thorium ratio, and the age of formation of the material. Lead sources retain the characteristics isotope signature of the ores from which they are derived and accordingly it is possible, at least in principle, to quantify anthropogenic versus natural sources of lead in the environment using lead isotope ratio measurements (Shirahata et al., 1980; Petit et al., 1984; Sturges and Barrie, 1987, 1989; Rosman et al., 1993).

The Pb stable isotope ratios are given in Table 4 and illustrated in Fig. 17. The increase of 207/206 ratios is well correlated with a increase of Pb concentrations. The 207/206 ratios in sediments below the depth of 40 cm, in which Pb originated mainly from the natural lithogenic fractions, represent to be quite stable (207/206 = 0.8352 and 0.8356, respectively). The first increase (207/206 = 0.8377) in the 207/206 ratio occurred at the depth of 29.5-30.5 cm where we observed a slight increase in Pb concentration and EFs (Fig. 6 and 8). The isotope ratio continue to increase (207/206 = 0.8426) to the depth of 23.5-24.5 cm. At the depth of 23.5-24.5 cm, on the other hand, the ratio decrease to 0.8400 in accordance with the decrease of EFs (nearly to the natural background level). The sharp increase in the 207/206 ratio occurred between the depths of 15.5-16.6 cm and 10.5-11.5 cm, which is in excellent agreement with the rapid increase in Pb concentration. The ²¹⁰Pb age ranges from the middle 1940s to the late 1950s. During that period, Pb emissions from the East Asia increased very rapidly with the

vast industrialization as shown in Fig. 16. The upward depth profile of less radiogenic gradient (less enriched in ^{206}Pb) of Pb isotopic composition in sediments can best be explained by a progressive dilution of natural occurring Pb ($^{207}/^{206} = 0.8354$ on average) by different Pb sources with lower $^{207}/^{206}$ ratios which is surely anthropogenic in origin.

To validate an input of distinctly different Pb sources, we can calculate the isotopic ratio of the anthropogenic sources by the simplified equation (Petit et al., 1984);

$$(207/206)_{\text{tot.}} \times (\text{ppm Pb})_{\text{tot.}} = (207/206)_{\text{anthr.}} \times (\text{ppm Pb})_{\text{anthr.}} + (207/206)_{\text{nat.}} \times (\text{ppm Pb})_{\text{nat.}}$$

where $\text{Pb}_{\text{anthr.}} = \text{Pb}_{\text{tot.}} - \text{Pb}_{\text{nat.}}$ and $\text{Pb}_{\text{nat.}}$ is the mean value (14.0 ppm) of Pb concentrations below the depth of 35 cm. The $^{207}/^{206}$ ratios of the anthropogenic Pb so calculated are shown in Table 5. It is evident that the $^{207}/^{206}$ ratios of anthropogenic Pb calculated on the basis of this simple two sources model is significantly different (much less radiogenic) than those of the total Pb concentrations in sediments. From our data, it is not possible to discriminate specific sources of anthropogenic Pb reaching Cheju Island, because there is no reliable information on the Pb stable isotope ratios in Pb produced during the past and the isotopic compositions present in sediments represent the mixed ratios of Pb derived from various sources such as coal combustion, non-metal production and alkyllead in petrol. At the depth

of 20–30 cm in sediments (^{210}Pb ages range from 1860s to 1920s), most of anthropogenic Pb pollutants must have come from coal combustion and non-metal production, because the introduction of alkyllead in gasoline started in 1930s in the world. Here we can have an idea that anthropogenic Pb pollutants emitted from coal combustion and non-metal production in the East Asia during this period had less radiogenic 207/206 ratios (Table 5). After 1940s, the 207/206 ratios of anthropogenic Pb are found to be rather more radiogenic than those before 1920s, in spite of the fact that the input of anthropogenic Pb pollutants to the study area increased by a factor of about 4 (Fig. 8). This means that anthropogenic Pb sources with more radiogenic 207/206 ratios become more or less dominant. One of the most plausible anthropogenic Pb sources which affected more radiogenic 207/206 ratios observed in the upper sediments (>20 cm) could be automobile combustion of alkyl-leaded gasoline. The use of leaded gasoline was a principle source contributing to the vast increase of Pb emissions to the atmosphere in Japan during the period of 1960s to the early 1970s, while automobile Pb emissions in China and Korea constituted still a minor portion, in comparison with Pb emission from non-metal production such as lead, copper and zinc (Table 3). It is unlikely that Japan is the biggest contributor to anthropogenic Pb deposition at Cheju Island, in view of the movement of air masses passing over this island. In addition, more radiogenic isotopic signatures are also observed at the depth of 12.5–13.5

cm and 15.5-16.5 cm in sediments, ranging from the middle 1940s to the late 1950s, during which Pb emissions from leaded gasoline were insignificant in three countries. Considering the facts mentioned above, it is suggested that more radiogenic Pb pollutants deposited at Cheju Island could not be attributed only to the use of leaded gasoline. In fact, the lead isotope ratio due to automobile emissions are reported to vary widely, depending on the use of alkyllead imported from the United States ($207/206 = 0.908$) and the U.K. ($207/206 = 0.824$) in Japan and Korea (Mukai et al., 1993). Therefore, the transient change of anthropogenic Pb from less to more radiogenic ratio would be caused in part by the use of coals and/or ores of non-ferrous metals imported to the East Asia and/or by refuse incineration, oil combustion for energy production, and steel and iron manufacturing which are also contributors to lead emissions (Nriagua and Pacyna, 1988). The isotopic signature observed in sediments clearly indicates that the excess Pb deposited after ~1880 is anthropogenic in origin and originated from various emission sources.

3.7 Change in the atmospheric sulphur deposition

From the isotopic composition observed in sediments, it is highly plausible that the coal combustion and non-ferrous metals production would be dominant sources of anthropogenic Pb emissions in the East

Asia. If this is the case, the anthropogenic sulphur, for which the burning of the fossil fuels and copper production are main sources, must have been emitted, transported and thus deposited to the study area. Nriagu and Coker (1983) showed that the recent changes in the sulphur contents of the sediments was related to the increasing flux of pollutant sulphur into the lakes.

Total sulphur (TS) and total carbon (TC) profiles in our sediments are found to be closely related (Fig. 18). It appears that most of the sulfide produced from SO_4^{2-} reduction is stored primarily as C-bonded S rather than as inorganic forms. Organic S has also been identified as an important product of SO_4^{2-} reduction in freshwater bogs (Brown, 1986; Wieder and Lang, 1988). Okada et al. (1990) found that dust surfaces loaded in the atmosphere of the East Asia play an important role in sulfate formation. That is, sulfate is sorbed and/or formed on the surfaces of wetted dust particles, and displace the carbonates during the transportation from the arid source regions in China to the Pacific. This indicates that TS/Al ratios could be meaningful for normalization of the increased flux of sulfate deposition, compared to the natural background level (Schell, 1986). In order to assess a temporal change of the atmospheric sulphur deposition to the study area, TS contents was normalized to Al measured at the same layer. As shown in Fig. 19, enrichment factors begun to increase from the depth of 25 cm, corresponding to the ^{210}Pb age dating of ~ 1900 . During this century, the

upwards increase is found to be rapid between 25 and 15 cm, representing that the atmospheric sulphur deposition increased by a factor of 4 from its preindustrial level. There is a close similarity of increasing enrichment factors of TS and Pb with depth in sediments (Fig. 8 and 19), as already found in lake sediments by Kokkonen and Tolonen (1987) and Giblin et al. (1990). Sedimentary record of sulphur increase is suggested to represent an increase of anthropogenic sulphur deposition flux in history, based on the evidence of sulphur isotopes (Nriagu and Coker, 1983; Kokkonen and Tolonen, 1987). The concentrations of sulphur in sediments may not have a straightforward relationship to atmospheric emission and deposition. Holdren (1984) has suggested that a downward migration of sulphur may take place in sediments and has estimated that the time of the onset of excess sulphur deposition should be cut in about half. If this is the case in our sediments, the estimated age of the beginning of increased sulphur deposition flux could be updated. However, it is not known in which kinds of sediment the sedimentary sulphur profiles do hold as a true historical record (Kokkonen and Tolonen, 1987).

Our data for sedimentary sulphur record support the suggestion that the changing atmospheric Pb flux observed in peatland sediments with time resulted undoubtedly from anthropogenic Pb pollutants emitted from China, Korea, and Japan and the main sources for Pb emission would be the burning of the fossil fuels and copper production. At present, it is

still difficult to assess quantitative contribution from China, Korea and Japan to the atmospheric flux of anthropogenic Pb deposited to the study area. We can assume that the relative impact of regional industrialization in three countries on the deposition of man-made Pb and S at Cheju Island may have varied with time, depending on the economic growth, demand of resources containing Pb, and introduction of efficient measures to control the emission of pollutants. While the historical record of atmospheric pollution for Pb in the East Asia is evidently observed from our study, it is needed to carry out further investigations at different sites for reconstructing the past regional cycles of most of the trace elements and monitoring environmental contamination.

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Table 1

Meteorological characteristics at Cheju Island. Data from Carmichael et al. (1996).

Month	Wind speed (ms^{-1})	Wind direction	Temperature ($^{\circ}\text{C}$)	Total precipitation (mm)
92-Feb.	7.7	N	6.9	159.0
Mar.	5.0	N-NE	10.1	134.4
Apr.	5.2	N-NNE; SE	13.7	115.4
May	4.2	NNW-NNE; S-SE	16.4	96.5
Jun.	3.5	N-ESE; SSE-SE	19.7	76.1
Jul.	3.5	SSE-S	26.0	92.0
Aug.	3.2	SSE-SE; N-NNE	26.1	326.6
Sep.	6.8	SSE-SE; N-NNE	23.1	133.6
Oct.	6.2	NNW-NNE	17.4	4.0
Nov.	6.7	N-NNE	12.6	56.6
Dec.	13.8	N	9.7	33.9
93-Jan.	11.5	N-NNE	5.4	32.8
Feb.	10.4	N	7.1	66.6
Mar.	7.9	NNW-N	8.9	90.7
Apr.	7.4	NNW-N; SE	12.5	23.6
May.	6.3	NNW-N; SE	16.4	132.3

Table 2

Various chemical compositions measured in sediments.

Depth (cm)	Bulk density (g/CC)	Ash content	Al	Ti	Fe (%)	TC	TS	Mn (ppm)	Pb
1	1.15	42.7	5.66	1.12	2.59	25.1	0.56	222	30.8
2	1.18	41.2	5.54	1.10	2.53	24.2	0.56	214	30.2
3	1.16	39.0	5.13	1.04	2.40	28.3	0.57	202	30.0
4	1.15	42.7	5.55	1.13	2.63	24.3	0.58	222	28.2
5	1.16	40.4	5.44	1.07	2.44	25.4	0.59	197	29.5
6	1.15	40.9	5.61	1.12	2.51	24.0	0.60	209	28.7
7	1.16	42.1	5.52	1.08	2.50	25.5	0.58	215	28.1
8	1.16	39.6	5.18	1.06	2.40	23.6	0.60	199	28.2
9	1.16	40.2	5.87	1.17	2.59	24.8	0.60	212	28.9
10	1.16	39.5	6.28	1.05	2.43	27.8	0.59	199	28.6
11	1.15	40.2	5.37	1.07	2.44	24.9	0.60	205	28.8
12	1.14	40.5	5.58	1.09	2.47	28.3	0.60	210	28.8
13	1.15	38.9	5.36	1.07	2.68	25.2	0.63	220	23.4
14	1.15	42.6	5.77	1.17	3.38	23.1	0.69	291	17.8
15	1.15	42.5	5.70	1.15	3.26	22.9	0.69	280	17.5
16	1.14	43.8	6.12	1.22	3.56	23.1	0.69	302	16.6
17	1.15	47.7	6.76	1.30	3.88	24.7	0.69	332	16.3
18	1.16	49.6	7.25	1.38	4.04	22.6	0.65	338	15.4
19	1.16	47.9	7.25	1.36	3.85	23.3	0.66	327	14.3
20	1.13	49.0	7.60	1.40	3.90	23.4	0.64	319	14.5
21	1.15	53.8	8.31	1.53	4.24	21.5	0.61	346	14.7
22	1.16	49.9	7.97	1.43	3.93	21.1	0.64	313	11.7
23	1.16	57.6	8.94	1.62	4.68	18.6	0.53	379	17.8
24	1.18	62.6	9.33	1.93	5.35	16.5	0.47	422	18.4
25	1.23	69.4	10.25	1.99	6.44	12.4	0.34	542	17.1
26	1.25	70.4	10.22	2.02	6.51	11.5	0.31	540	16.8
27	1.23	73.4	10.95	2.11	6.83	11.2	0.30	557	16.4
28	1.22	69.1	10.60	2.06	6.45	12.3	0.34	509	16.9
29	1.22	69.0	10.38	2.03	6.32	12.1	0.34	508	17.5
30	1.22	69.1	10.74	2.09	6.36	12.7	0.34	509	17.1
31	1.22	68.6	10.80	2.07	6.33	13.0	0.37	489	
32	1.21	67.6	10.36	1.99	6.10	13.2	0.37	477	15.3
33	1.21	69.4	10.49	2.03	6.28	12.6	0.36	500	
34	1.22	69.9	11.25	2.07	6.37	11.6	0.35	487	13.2
35	1.20	67.1	10.52	1.94	5.92	13.1	0.38	452	

Table 2. Continued.

Depth (cm)	Bulk density (g/CC)	Ash content	Al	Ti	Fe (%)	TC	TS	Mn (ppm)	Pb
36	1.20	69.9	10.90	1.99	6.12	12.2	0.35	460	14.6
37	1.18	67.9	10.37	1.92	5.93	13.1	0.36	468	
38	1.18	67.6	10.48	1.91	5.81	13.6	0.38	445	14.1
39	1.19	66.8	10.15	1.88	5.82	13.6	0.37	440	
40	1.17	66.0	10.10	1.89	5.82	14.3	0.39	460	13.8
41	1.18	64.7	9.80	1.90	5.82	14.9	0.40	461	
42	1.17	61.2	9.25	1.80	5.53	17.3	0.44	436	13.0
43	1.15	58.5	9.05	1.78	5.43	19.5	0.48	449	
44	1.16	62.4	9.15	1.89	5.89	16.9	0.42	483	
45	1.19	66.9	10.24	2.29	6.54	13.8	0.34	518	13.7
46	1.22	69.6	11.62	2.13	6.72	12.2	0.29	536	
47	1.22	70.4	10.36	2.22	6.98	11.7	0.27	562	
48	1.23	70.5	10.03	2.16	6.87	11.6	0.27	579	14.4
49	1.22	71.8	10.32	2.23	7.11	11.6	0.27	589	
50	1.24	72.6	10.29	2.26	7.19	11.5	0.27	602	
51	1.24	71.0	9.69	2.13	6.79	11.6	0.27	567	13.7
52	1.24	70.8	9.98	2.19	6.88	11.8	0.27	570	
53	1.25	71.9	10.06	2.19	6.94	11.3	0.27	579	
54	1.25	71.8	10.07	2.22	7.00	11.3	0.26	573	13.9
55	1.25	71.2	9.78	2.14	6.76	11.3	0.25	562	
56	1.24	72.2	9.94	2.19	7.03	11.2	0.26	593	
57	1.26	71.7	9.67	2.15	6.98	11.6	0.26	594	13.6
58	1.25	72.4	10.01	2.19	7.21	11.5	0.25	623	
59	1.27	72.6	10.14	2.19	7.21	11.0	0.24	635	
60	1.27	72.8	9.93	2.18	7.06	10.9	0.24	604	15.0

Table 3

The amount (tonne/yr) of Pb emitted to the atmosphere from various sources with ages. The abridged characters, C, K, and J mean China, Korea, and Japan, respectively.

Year	Pb+Cu+Zn			Coal			Gasoline		
	C	K	J	C	K	J	C	K	J
1910	-	-	770	150	-	180			
1915	100	10	850	175	3	240			
1920	250	30	1300	240	3	340			
1925	300	25	1370	280	7	370			
1930	410	25	1650	300	10	370			
1935	535	80	1780	460	17	440			
1940	640	380	2640	550	45	660			
1945	320	100	1120	290	8	260			
1950	550	-	1090	500	<1	495	Nil	Nil	140
1955	1460	70	1960	1060	30	555	10	30	800
1960	5400	620	3400	4100	60	650	20	100	1760
1965	4100	1050	6000	2400	100	680	50	155	3260
1970	4300	900	6400	2800	100	750	90	560	5500
1975	5900	1400	7000	3800	140	680	240	420	440
1980	5900	1000	5600	4700	200	660	380	710	115
1985	8000	1400	6100	6300	310	850	465	975	Nil
1990	11600	2000	6800	8000	335	930	595	310	Nil

Table 4

Pb isotope compositions determined in sediments.

Depth (cm)	206/204	207/204	208/204	207/206
2.5-3.5	18.369	15.688	38.731	0.8541
6.5-7.5	18.366	15.655	38.656	0.8524
10.5-11.5	18.341	15.624	38.531	0.8519
12.5-13.5	18.398	15.639	38.655	0.8501
15.5-16.5	18.581	15.661	38.936	0.8429
21.5-22.5	18.653	15.668	39.027	0.8400
23.5-24.5	18.597	15.669	38.968	0.8426
29.5-30.5	18.690	15.657	39.075	0.8377
41.5-42.5	18.728	15.643	38.976	0.8352
53.5-54.5	18.747	15.666	39.078	0.8356

Table 5

207/206 ratios of the excess Pb in sediments. "Total" means the ratios measured in the bulk sediments and "excess" in the anthropogenic portions calculated from the natural level in deeper layers.

Depth (cm)	207/206 (total)	207/206 (excess)
2.5-3.5	0.8541	0.8602
6.5-7.5	0.8524	0.8590
10.5-11.5	0.8519	0.8579
12.5-13.5	0.8501	0.8573
15.5-16.5	0.8429	0.8514
21.5-22.5	0.8400	1.1045
23.5-24.5	0.8426	0.8619
29.5-30.5	0.8377	0.8600

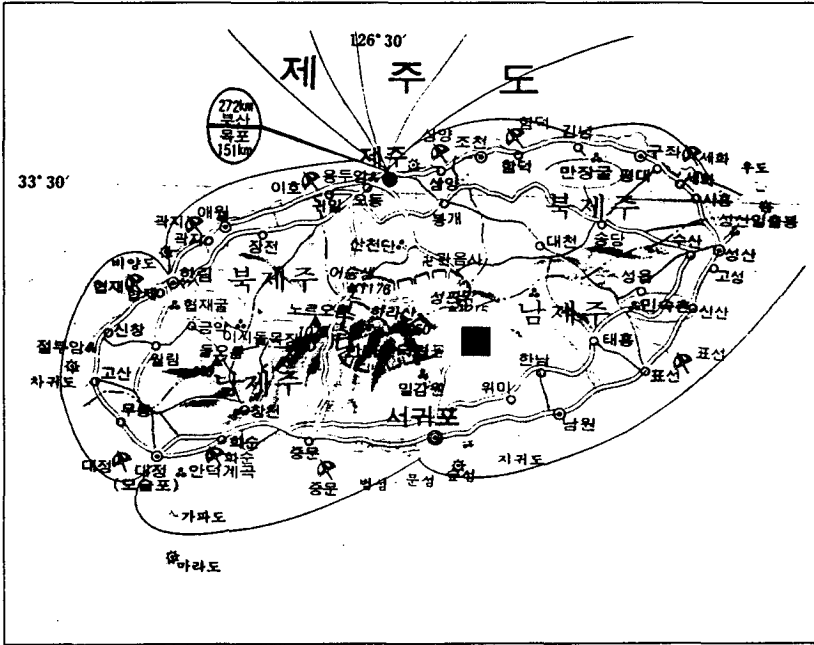


Fig. 1. Map of the sampling site.

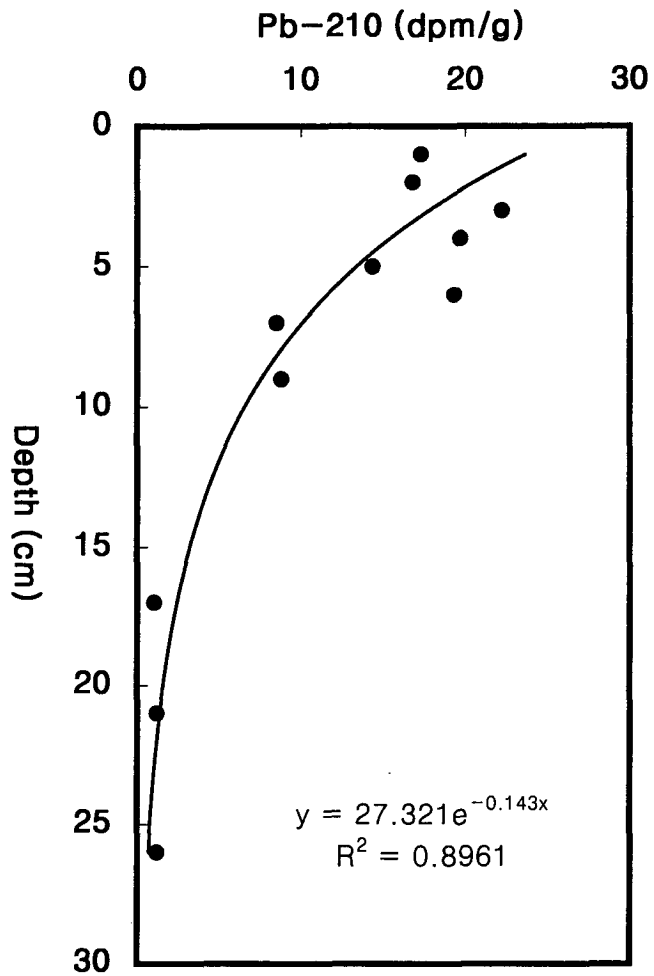


Fig. 2. Vertical profile of Pb-210

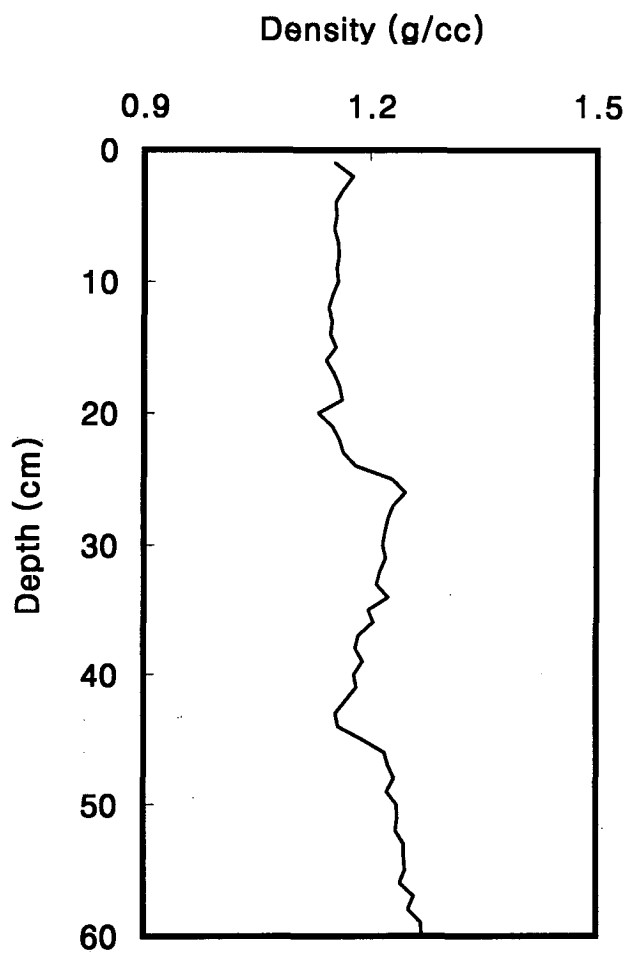


Fig. 3. Variation of bulk density with depth

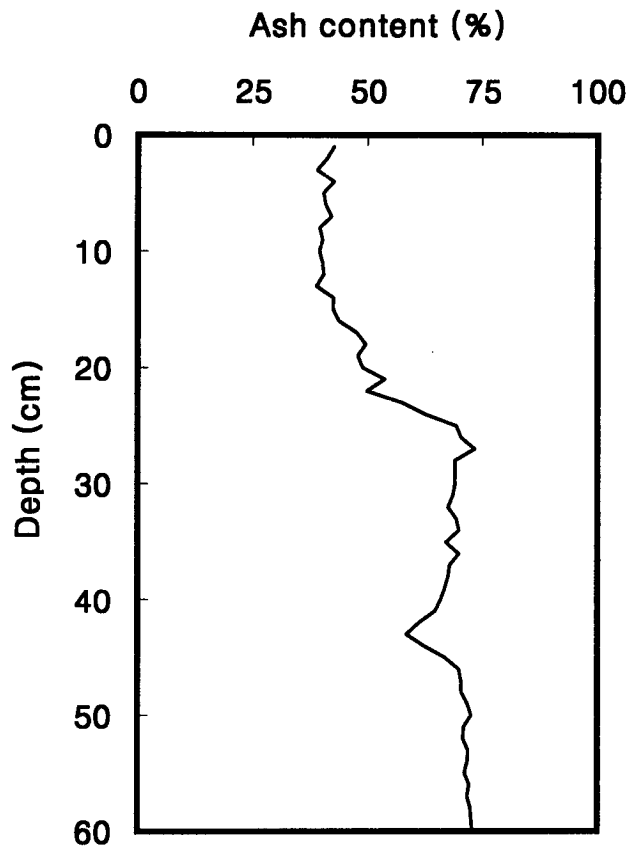


Fig. 4. Variation of ash content with depth

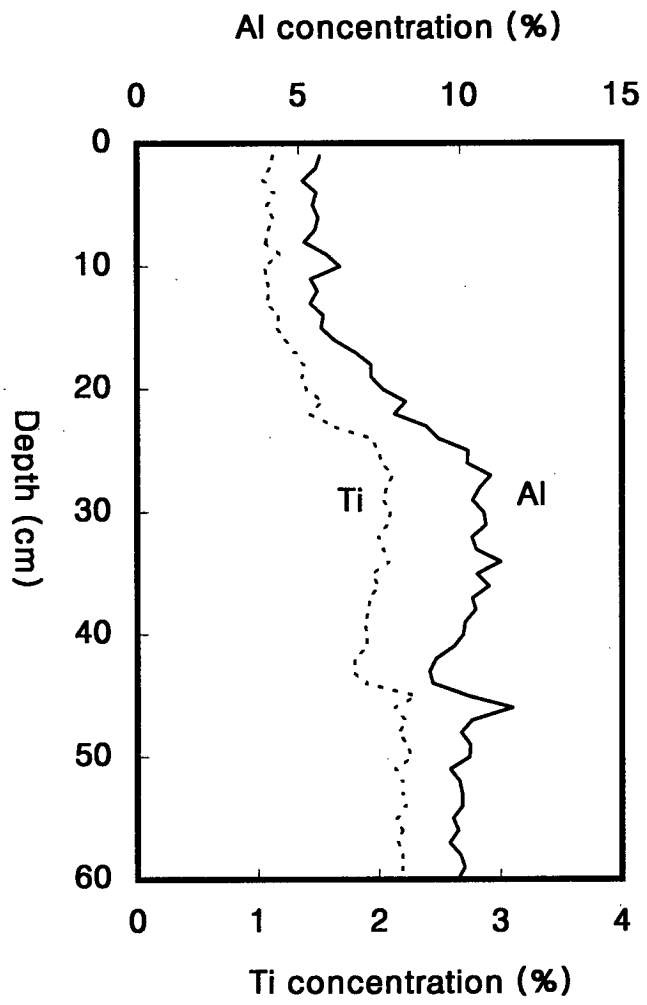


Fig. 5. Variations of Al and Ti concentrations with depth

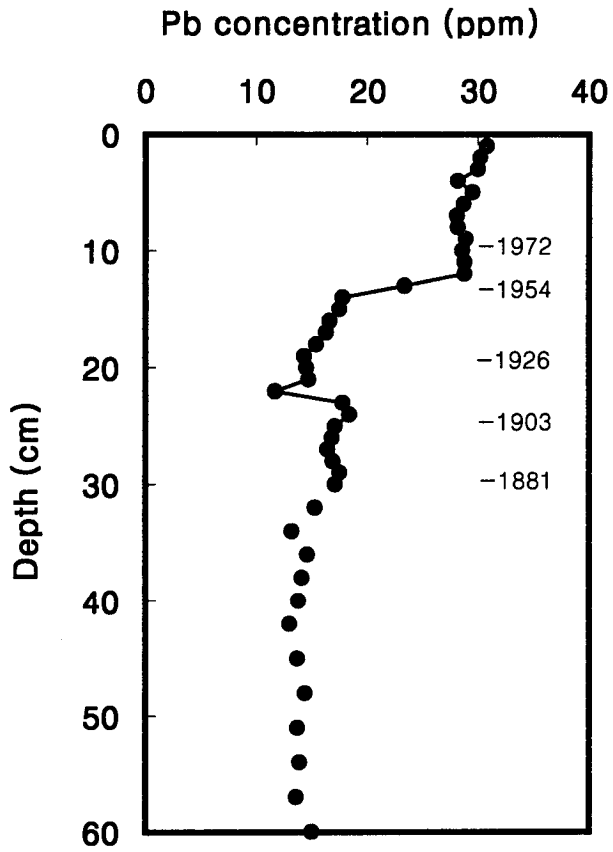


Fig. 6. Variation of Pb concentrations with depth

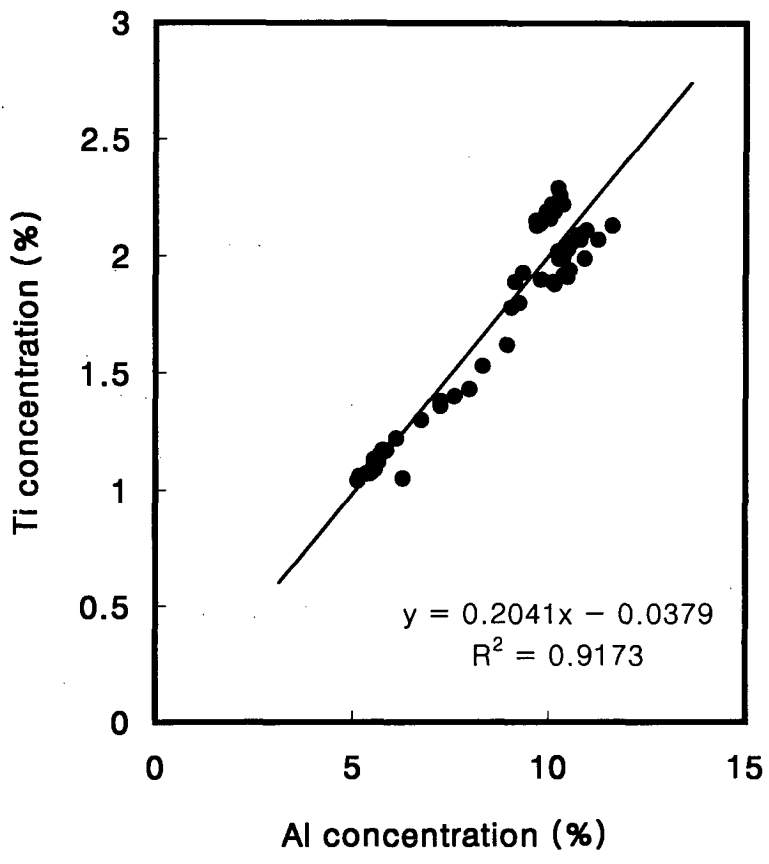


Fig. 7. Correlation between Al and Ti contents

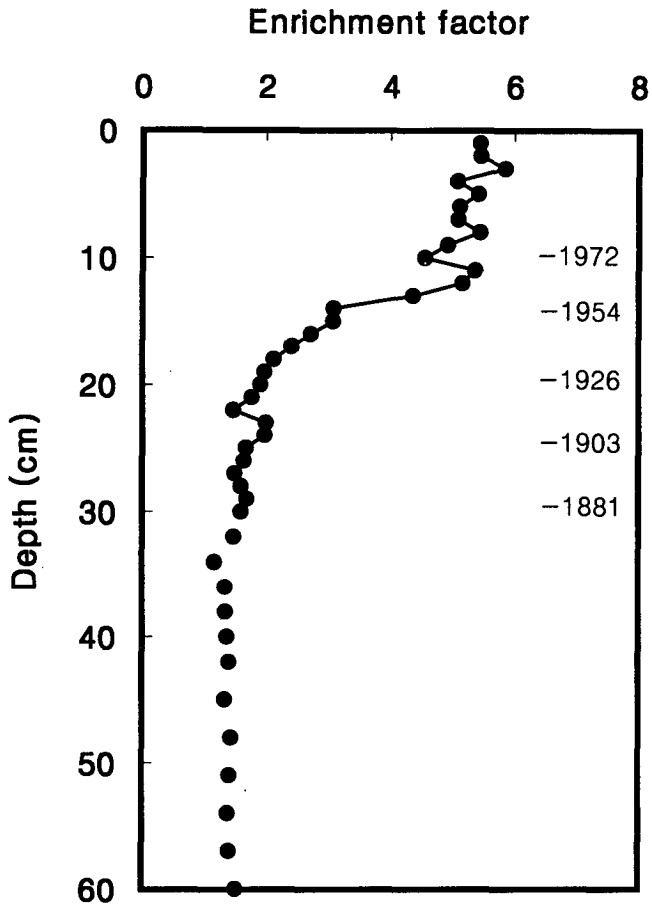


Fig. 8. The depth profile of enrichment factors of Pb

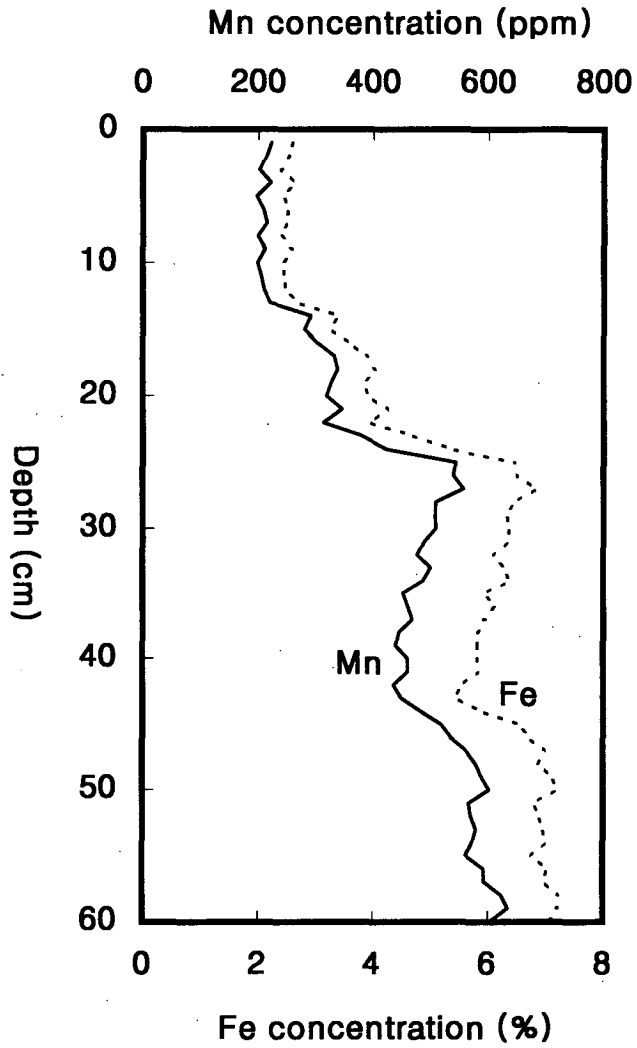


Fig. 9. Variations of Fe and Mn concentrations with depth

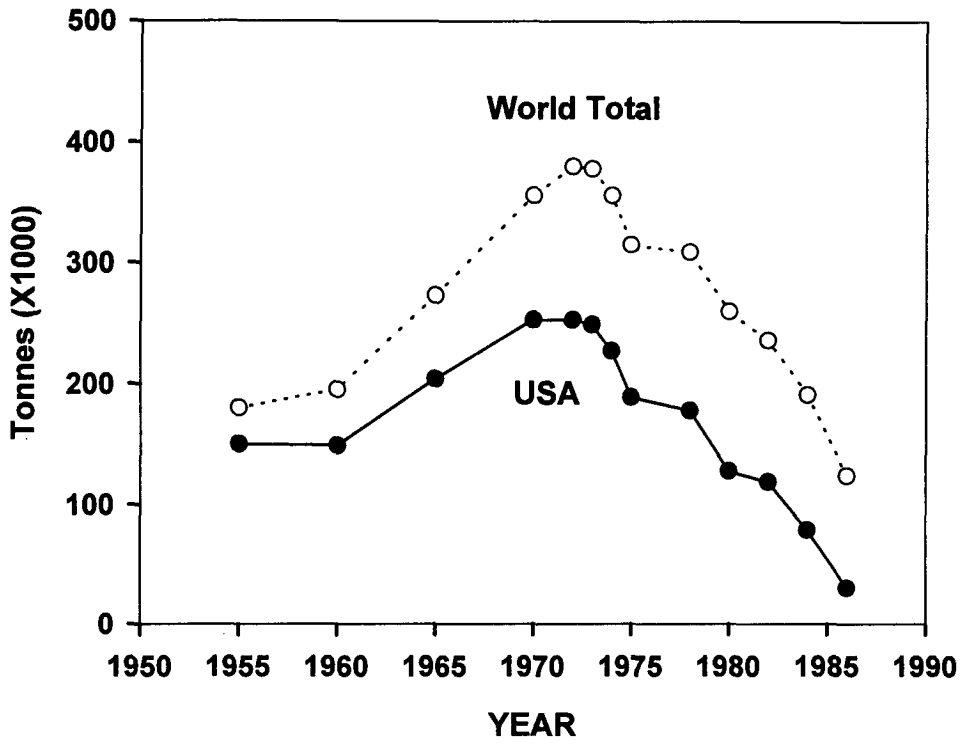


Fig. 10. Consumption of lead for gasoline additives in the United States and in the world

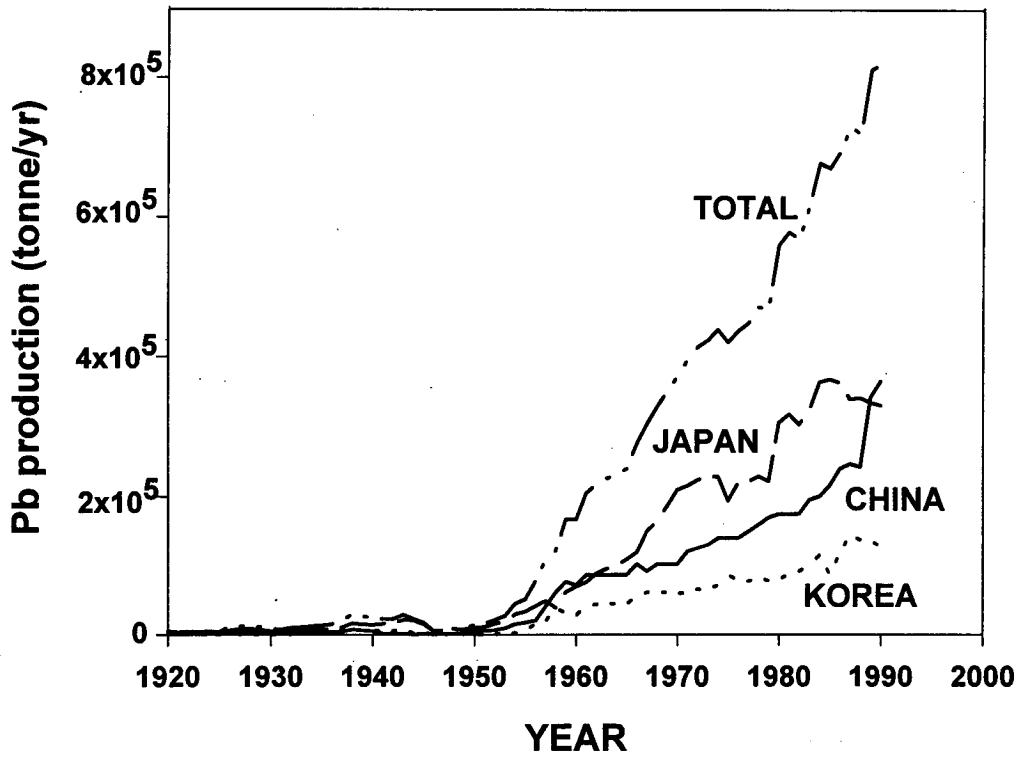


Fig. 11. Historical Pb production rates in China, Korea and Japan

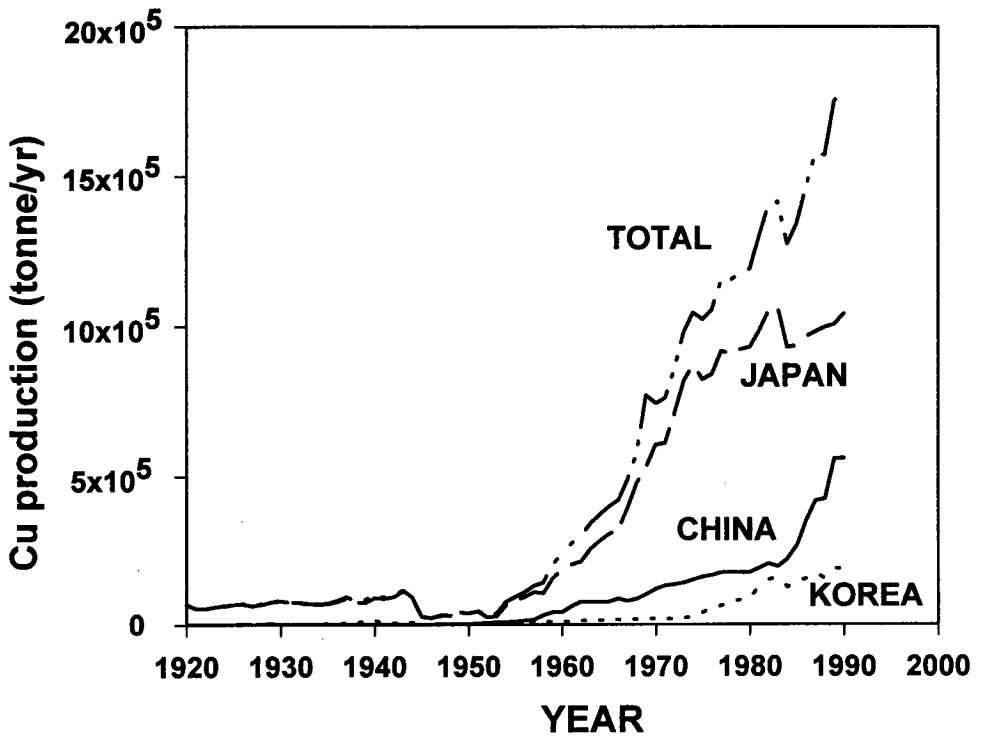


Fig. 12. Historical Cu production rates

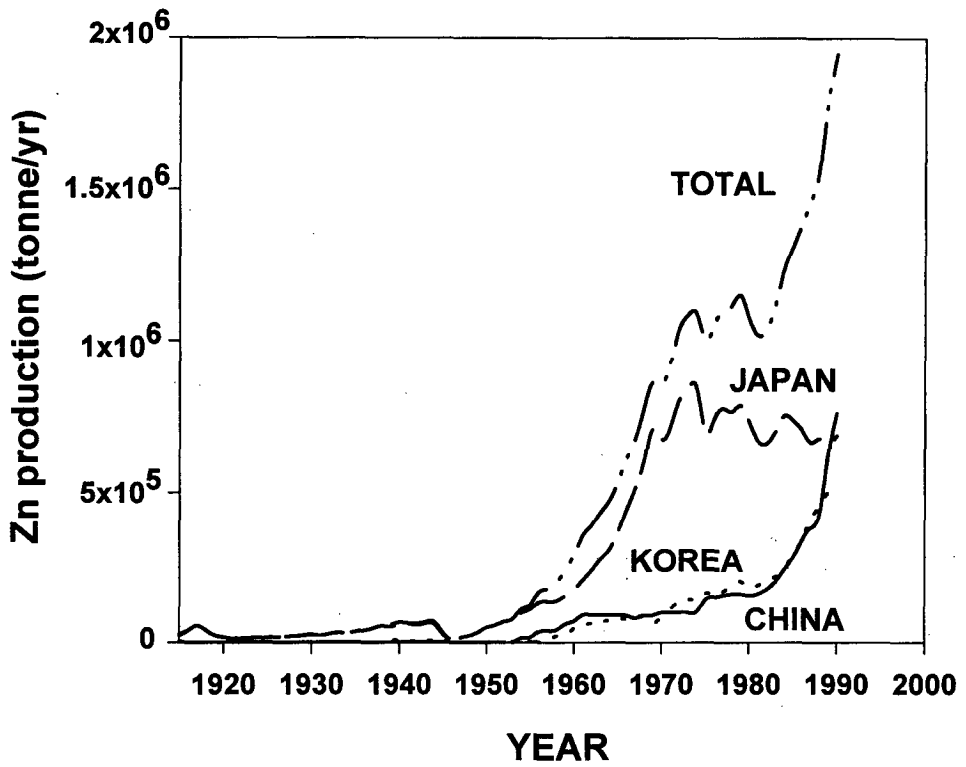


Fig. 13. Historical Zn production rates

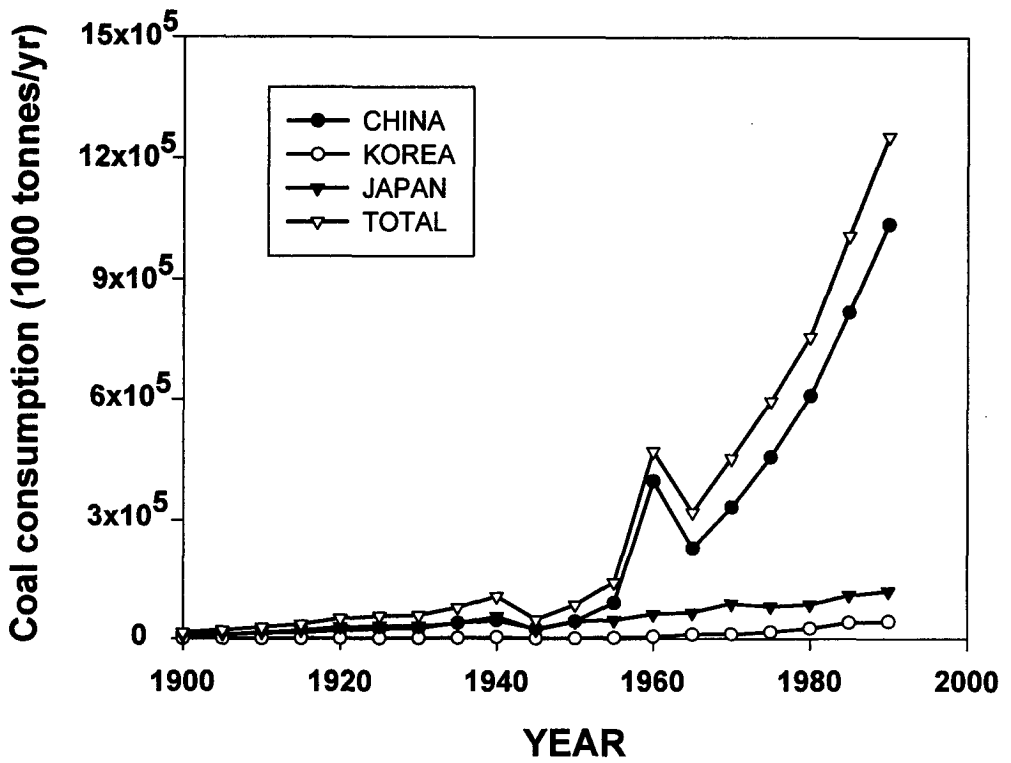


Fig. 14. Historical coal consumption in China, Korea and Japan

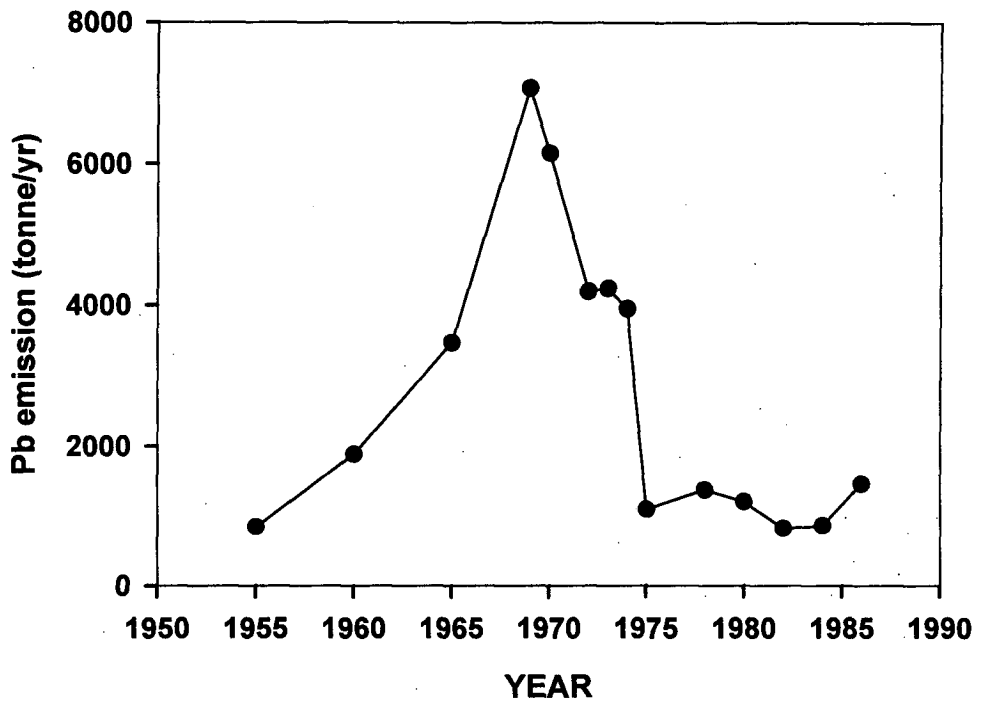


Fig. 15. Pb emissions from the use of leaded gasoline

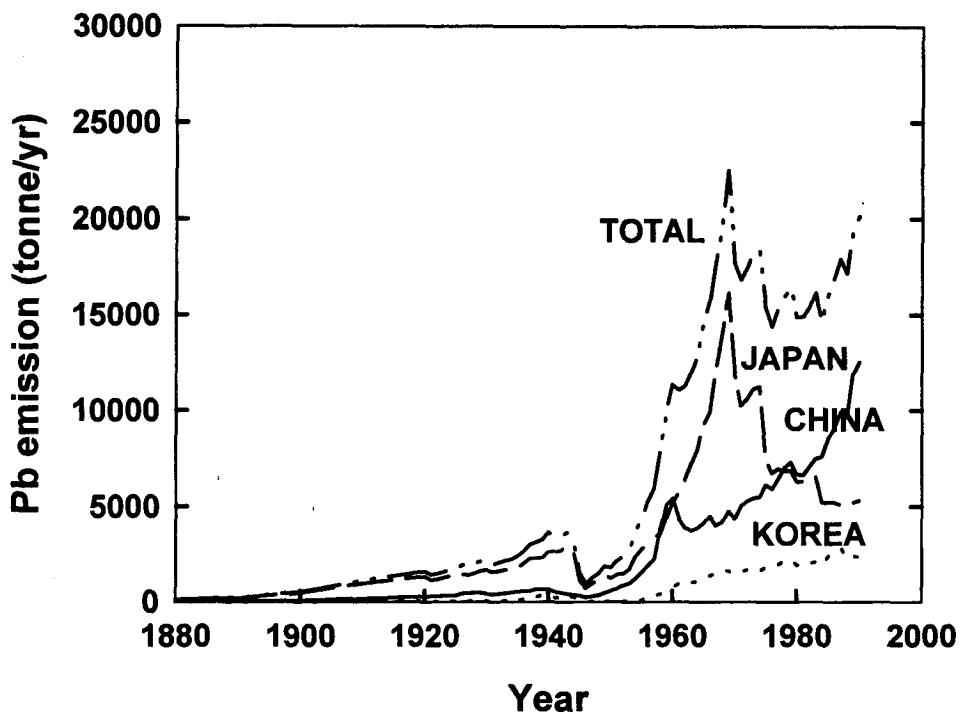


Fig. 16. Time trend of total Pb emissions from various sources

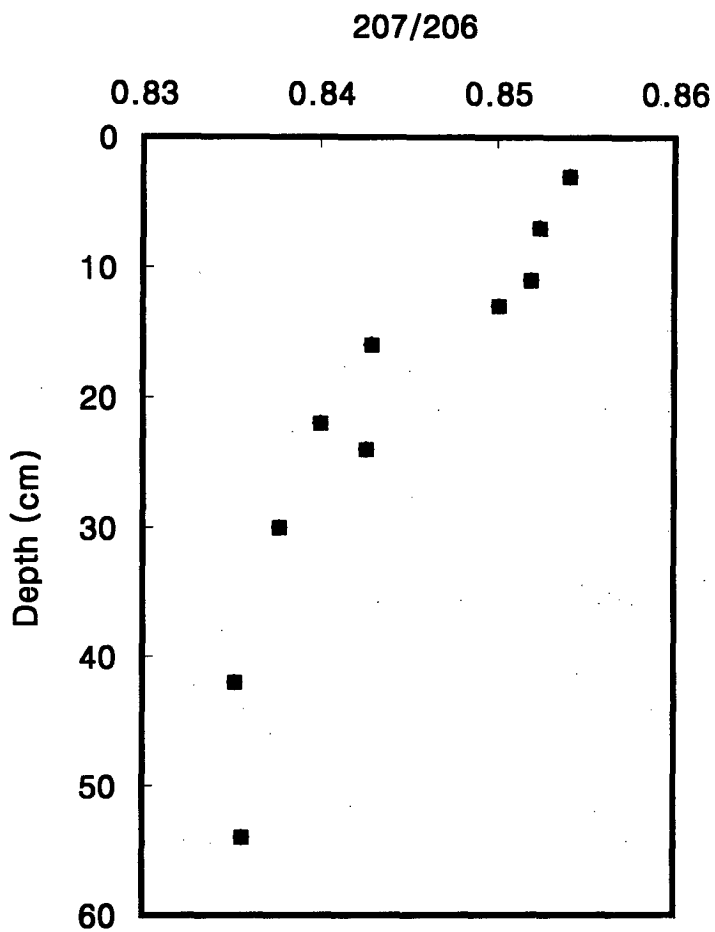


Fig. 17. Variation of Pb stable isotope (207/206) with depth

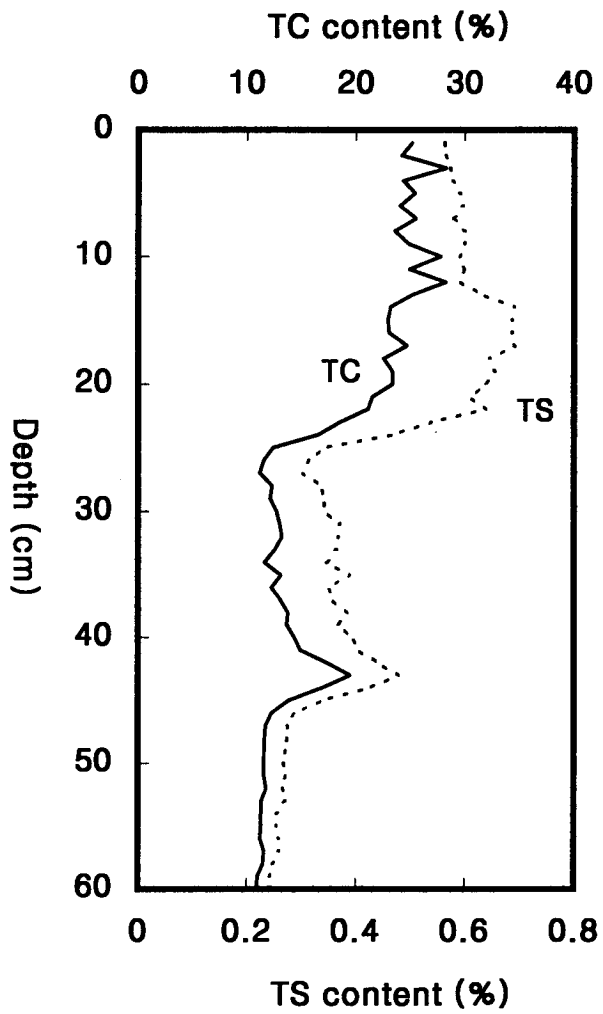


Fig. 18. Variation of TS and TC contents with depth

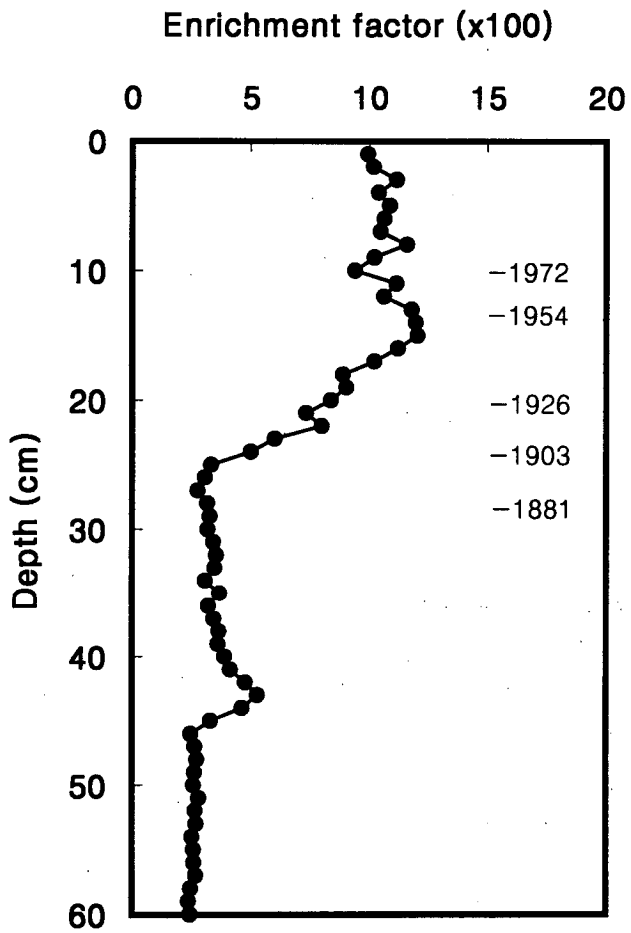


Fig. 19. The depth profile of enrichment factors of TS