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Historical trends of polycyclic aromatic hydrocarbons in the reservoir sediment core at Osaka

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Abstract

The historical trends of polycyclic aromatic hydrocarbons (PAHs) in the sediment core of the moat in Osaka Castle, located at the center of Osaka city, Japan, were studied. The moats in Osaka Castle were built in the 1620s, and the undisturbed sediment core, which consists of atmospheric deposits in Osaka city from 1671 to 1976, was withdrawn from the moat. PAHs in the sediment core were identified and quantified in the total concentration range of 0.053–26 mg kg^{-1} dry wt. The highest content of PAHs was found in the sample, which was dated to 1944 during World War II. Osaka Castle was exposed to intense bombing raids during World War II, and the spiked peak of the PAH concentration during the mid-1940s was due to the air attacks. The total PAH concentration in the sediment core sample during World War II was about two-fold greater than the average after the war. This study made it appear that the largest impact of PAHs on the atmospheric environment in Osaka city in almost 300 years was caused by modern warfare.

Keywords: Osaka Castle; Moat; Deposit; World War II; Polycyclic aromatic hydrocarbon

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1. Introduction

Osaka city, located approximately at the center of Japan, is a metropolis. The population of Osaka city has been over 0.4 million since the 17th century and almost 2.5 million in 2001. Osaka Castle was built in the 1620s at the center of Osaka city. The buildings of Osaka Castle were struck by lightning and burned several times during wars (Table 1). On the other hand, the moats in the castle are of the same structure at the time it was built in the 1620s and have been maintained as historical monuments. The sediment in the moat consists of dust from the atmosphere because there is no inflow and outflow of water. Furthermore, the deposit has not undergone any artificial treatment, such as dredging, for almost 400 years.

We took an undisturbed sediment core from the outer moat of Osaka Castle. The features of this sediment core are as follows: (i) the sample is a historical record of the atmospheric environment at the center of this large metropolis from pre-industrial times to recent years, and (ii) there are detailed records of historical accidents and economic changes in its surroundings.

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Table 1
A chronological table for Osaka Castle

Year	Historical accidents and backgrounds
1620s	The construction of the outer moat of Osaka Castle was completed.
1660	A thunderbolt hit an explosives warehouse in Osaka Castle, resulting in an explosion.
1665	The main tower was struck by lightning, resulting in its destruction by fire.
1783	Turret of Otemon, which was the main gate of Osaka Castle, was destroyed by fire.
1868	Most of the castle structures were burned in an internal war, called Toba-Fushimi War.
1890s	Industrial revolution in Japan.
1931	The reconstruction of the main tower.
1941–1945	The castle was exposed to bombing raids during World War II, resulting in the destruction of four buildings in the castle.
1960s	The transition period from coal to oil.

In this study, polycyclic aromatic hydrocarbons (PAHs) in the sediment core of the moat were investigated. PAHs are ubiquitous contaminants of great environmental concern. They are by-products from the incomplete combustion of fuels and wood, and the PAHs persist in the environment (Mastral and Callen, 2000). Some of the PAHs, such as benzo[*a*]pyrene (B(a)P), have a high carcinogenicity (Bostrom et al., 2002), and the concentrations of the PAHs in the atmosphere are regarded as indicators of air pollution (Pertry et al., 1996). Therefore, the historical trends of PAHs recorded in the sediment core from the moat at Osaka Castle should reflect the changes in the atmospheric pollution in Osaka city.

The objectives of this study are to determine the changes in the metropolitan atmospheric environment over almost 300 years and to explore how the temporal changes in human activities and historical accidents have affected the atmospheric environment.

2. Experimental

2.1. Sediment sample

A sediment sample was obtained from the outer moat of Osaka Castle (Fig. 1). The sampling was performed using normal gravity coring equipment from a raft floating on the moat. The sediment core was about 2 m long. The sample was dried at room temperature and stored in a dark place. Thirty-one samples at various depths were used for the determination of the PAHs. The dating of the core samples was estimated using the depth profile of ^{137}Cs activity and the speciation and the distribution of charcoal (Yamazaki et al., 2003). The sediment core consists of the deposit of Osaka city during almost these 300 years (1671–1976). The dating of the core sediments was estimated by a ^{137}Cs method. The concentration profile of the ^{137}Cs is effectively used as a time marker of the core sediment (Robbins and Edgington, 1975; Goldberg et al., 1976; Spleithoff and Hemond, 1996; Yasuhara et al., 2003). In Japan, the atmospheric fallout of ^{137}Cs was detected from the beginning of the 1950s, and the maximal value was shown in 1963 (RSD, 1963). The age of the deepest depth where ^{137}Cs was detected in the core corresponds to the beginning of the 1950s, and the depth to which ^{137}Cs shows the highest concentration in the core is in the year 1963, year in which the fallout became maximum.

2.2. Analytical techniques

An analysis of the PAHs was performed according to a modification of the procedure reported by Tsuji et al. (1985). It is briefly summarized as follows. The 0.5 g sediment samples were extracted by ultrasonic agitation. A 30 min extraction was carried out in a centrifuge tube with ethanol (4 ml) and toluene (16 ml), and then the tube was centrifuged at 1500 rpm for 10 min. This treatment was repeated two times. The supernatants were combined and concentrated to 1 ml by a rotary evaporator, and then dried by a flowing N_2 stream. The residue was dissolved in *n*-hexane (2 ml). The hexane solution was loaded onto a Sep-Pak Plus silica cartridge (Waters). The cartridge was eluted with 10 ml *n*-hexane/toluene (90:10, v/v) into a glass tube. The eluent was dried by a nitrogen purge and dissolved in 0.5 ml acetonitrile. A 40 μl acetonitrile solution was injected into the HPLC.

The quantification of the PAHs was performed using an HPLC/fluorescence detector. Chromatograms were obtained from an HP 1100 interfaced with a fluorescence detector (Hewlett Packard). The HPLC system was equipped with a Supelcosil LC-PAH (Supelco) reverse-phase C18 column (4.6 × 250 mm, 5 μm particle size). Sample aliquots and the calibration standard (40 μl) were injected using an auto sampler. The flow rate was 1.0 ml/min. As the mobile phase, a water/acetonitrile gradient was employed as follows: 5 min acetonitrile 50%; in 30 min to 100% acetonitrile held for 15 min. With the fluorescence detector, excitation was set at 270, 245, 260 and 297 nm and emissions at 333, 350 and 430 nm.

The following nine PAHs were detected and determined in this study: phenanthlene (Phe), fluoranthene (Flu), pyrene (Py), benz[*a*]anthracene (B(a)A), chrysene(Chr), benzo[*b*]fluoranthene (B(b)F), benzo[*k*]-fluoranthene (B(k)F), benzo[*a*]pyrene (B(a)P) and