B−49 Origin and distribution of PAHs in port and harbor sediments: A comparative study of two harbors in Norway and Nagoya Port, Japan

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1. INTRODUCTION

Both Japan and Norway have economies and histories that strongly center on their extensive coastlines and relationship with the sea. The many urban centers, industrial areas and energy generation plants located on or near their coasts has in turn led to various levels of harbor contamination as well as fishing, industrial and recreational restrictions in certain areas. Both countries are confronted with the challenge of better assessing the impacts of such pollution, its distribution and ultimately the ecological recovery of their harbors.

This paper presents a joint Japanese-Norwegian collaborative study to compare trends and sources of one of the most predominant contaminants, polycyclic aromatic hydrocarbon (PAH), in two Norwegian harbors, Oslo and Drammen, and one Japanese harbor, Nagoya. Typical PAH sources in these harbors are manufactured gas plants (MGP), metal smelters, vehicle emissions, creosote wood impregnation and petroleum. A previous study in Oslo harbor[1] on historical industrial activities and contaminant profiling in sediment cores concluded that legacy MGP pollution is the major source of PAHs. Though PAHs are known to be in substantial levels in Drammen and Nagoya, there main source remains uncertain. Here we conduct an analysis of PAH and metal analysis, to compare similarities and differences in the potential sources, distribution behavior, bioavailability and trends in core samples.

2. MATERIALS AND METHODS

In Oslo harbor, four sediment cores (from 20–84 cm in depth) were taken in well-distributed areas between 2005 and 2008. Cores were sliced in 2–5 cm intervals. More details about the field campaign are presented elsewhere[1]. In Drammen harbor, thirty sediment cores (0–10 cm) were taken from six well-distributed areas in 2008. In Nagoya 35 surface samples, including 4 cores, were taken from diverse regions throughout the port in 2007.

PAHs in Oslo and Drammen sediment were extracted with acetone-heptane reflux extraction, and quantified with GC/MS. In Nagoya, PAHs were extracted from sediments with heated 1M KOH / ethanol, cleaned up with silicagel and quantified with GC/MS.

Metals in Oslo sediment were extracted with HNO_3 in an autoclave, for Drammen with HNO_3/peroxide mixture and in Nagoya with HF. Quantification was done with an ICP-AES for Oslo and Drammen sediment, and with ICP-MS for Nagoya sediment.

For data comparision, PAH analysis from 14 MGP sites, 3 aluminum sites, and 2 urban harbors in the U.S. were taken from a recent study[2]. Additionally, PAH ratios for 2 petroleum mixtures were taken for comparison[3]. A weathering index for PAHs was calculated based on the ratio of high molecular weight to low molecular weight PAHs in the U.S. EPA-16 list, as W_{EPA-16} = (4+5+6 ring PAHs) / (2+3 ring PAHs)

Toxicity is estimated based on a recent method that relates toxicity from complex PAH mixtures to pyrene concentrations.[2] This method was validated using over 200 sediment samples to be as accurate

directly measured porewater concentrations of the U.S. EPA-34 list of PAHs and alkyl PAHs for estimating acute toxicity to benthic anthropods.

$$\log TU = 1.18 \log\left(\frac{C_{sed,pyrene}}{f_{TOC}K_{TOC}FCV}\right) + 1.82 \qquad (1)$$

Where TU is the toxicity unit (log TU = 0 implies that 50% survival is expected), $C_{sed,pyrene}$ is the pyrene concentration (μg/kg), f_{TOC} is the mass fraction of total organic carbon (TOC) in the sediment, K_{TOC} is the TOC-porewater partitioning coefficient ($10^{6.06}$ for pyrene), and FCV is the U.S. EPA final chronic value (10.1 μg/L for pyrene).

3. RESULTS AND DISCUSSION

(1) PAH distribution

The average relative distribution of 12 PAHs in surface sediments from the three harbors is presented in **Figure 1** (as it was these 12 PAHs that were measured in all three harbors). As is evident, the relative distribution of these 12 PAHs are quite similar, and not statistically different for the most part. The most abundant PAHs are fluoranthene and pyrene in all three harbors, which is typical for pyrogenically produced PAHs.

(2) Comparison with MGP, Aluminum Smelter and Petroleum polluted sediments.

The average relative PAH distribution in each harbor is compared with those of MGP and aluminum smelter polluted sediments as well as petroleum in Figures 1a, 1b and 1c respectively. The differences in the relative percentages are most different from petroleum (**Figure 1c**), pointing to petroleum not being the predominant PAH source. For MGP (**Figure 1a**), the predominant PAHs are also flouranthene and pyrene, and the differences between the distribution patterns are not statistically significant, for the most part. For aluminum smelters (**Figure 1b**), there is an evident enrichment of larger PAHs, with indeno-(1,2,3-cd)-pyrene being the most abundant. Though some relative abundances are significantly different, most are similar.

(3) Weathering Ratios

As presented in **Table 1**, the average W_{EPA-16} ratios for Drammen and Nagoya are not significantly different (W_{EPA-16} was not available for Oslo). However, these values are significantly larger than for MGP sites and significantly less than aluminum smelter sites. Aluminum smelter sites are generally depleted in low molecular weight PAHs. Based on

this comparison in **Table 2**, the source of PAHs is consistent with a mixture of different sources, or an MGP site in which low molecular weight PAHs have been depleted (or weathered) away. Similar W_{EPA-16} values were also found for two urban harbors in the U.S. (2), indicating these results could be typical for urban harbors with diverse mixed sources such as MGP and vehicle emissions.
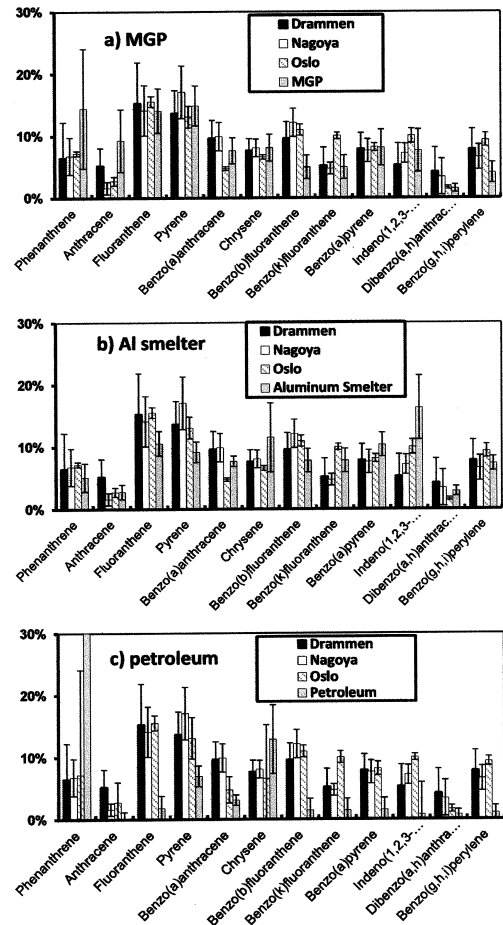

Fig.1 Comparison of relative PAH abundance in Drammen, Nagoya and Oslo with values for MGP, Aluminum smelter and petroleum contamination.

Table 1 PAH weathering ratios in Drammen and Nagoya compared with other contaminated sites[2].

W_{EPA-16} (-)	average	std. dev.
Drammen	6.6	2.4
Nagoya	6.4	2.9
MGP	2.8	2.1
Al-smelter	11.0	6.7
Urban	5.1	1.6

(3) PAH, TOC and metal correlations

Correlation coefficients (r^2) for log-normalized PAH, Cd, Cu, Pb, Zn and TOC concentrations for all

cores and depths are presented in **Table 2**. Close correlations indicate a similar spatio-temperal pollution source. Decent to good correlations of all contaminants (r^2 from > 0.5) were observed in Oslo and Nagoya, but correlations were very poor in Drammen. This indicates the pollution sources were more chaotic and diffuse in the case of Drammen. Close correlations between Pb and PAHs are typical for MGP or coal burning plants[1]. Though good r^2 values were present for Oslo and Nagoya, this does not necessarily imply similar sources for these contaminats, but only similar spatio-temporal occurance.

Table 2 r^2 of log-log correlations of C_{PAH-12} vs. metals or TOC

r^2	TOC	Cd	Cu	Pb	Zn
Drammen	0.00	0.04	0.00	0.01	0.01
Nagoya	0.62	0.55	0.61	0.57	0.60
Oslo	0.76	0.85	0.83	0.87	0.76

(4) PAH Toxicity comparison

The average, maximum and minimum toxicity (following eq 1) of all surface sediments (0 – 5 cm) is presented in **Table 3**. From this analysis, Nagoya samples exhibited the highest range and most PAH toxicity, and Drammen exhibited the lowest. With this model, pyrene concentrations around 10 mg/kg (depending on the f_{TOC} value) will result in a log TU value of 0, which indicates roughly 50% of benthic anthropods will not survive (based on acute PAH toxicity). The majority of surface sediments were below this, except for some sediments in Nagoya.

Table 3 Toxicity (log TU) of surface sediments

log TU	Average	Max	Min
Drammen	-1.86	-0.75	-2.73
Nagoya	-1.15	0.08	-2.42
Oslo	-1.38	-0.86	-1.72

(5) Trends in Core Samples

Fig. 2 shows the average total 12 PAH concentration in (approximately) 0–5 cm and 5–10 cm sediment core depths in the three harbors, from the sediment core samples (n = 29 for Drammen, n = 4 for Nagoya, n = 4 for Oslo). As is evident from this figure, in all three harbors there is a trend for decreasing PAH concentrations in the upper layers. In the case of Oslo, which has traffic and legacy contaminated sites as the main PAH source (there has been no or little coal burning in Oslo since the 1960s), this was previously hypothsezied to be accountable to increasing regulations on vehicle and industry emissions in Norway[1]. This hypothesis likely also applies to Drammen, as such regulations are nation wide.
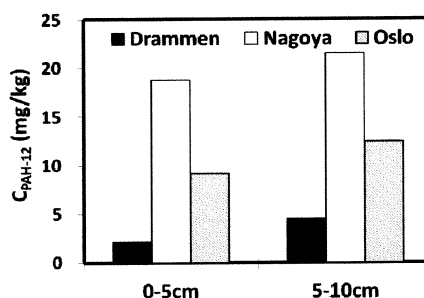

Fig.2 Comparison of average 0–5 cm and 5–10 cm sediment depth PAH-12 concentrations in Drammen, Nagoya and Oslo.

(6) Variability

The presented comparison of three harbors was mainly focused on general or average trends. The study ignored differences in errors or biases due to experimental methods (particularly extraction techniques, which can cause significant variations in reported concentrations) and sampling strategies (particularly the frequency of samples in highly contaminated and low contaminated areas). These biases may have caused systematic errors, particularly in the reported concentrations and estimated toxicity levels. Despite methodological differences, the consistency of the general trends, or lack there of, are unaffected.

5. CONCLUSIONS

Nagoya, Oslo and Drammen have similar relative PAH-12 distribution and W_{EPA-16} values, indicating the diffuse PAH sources in these urban harbors ultimately lead to a similar PAH signature. PAH concentrations are also gradually decreasing, perhaps due to more stringent regulations, which is a positive sign. More collaboration between Norway and Japan is needed to better understand trends in sediment pollution in these and other countries.

REFERENCES
1) Arp, H.P.H., et al.: Influence of Historical Emission Patterns on Porewater and Partitioning Profiles of PAHs and PCBs in Oslo Harbor Sediment Cores, *Environ. Toxicol. Chem.*, Vol. 30, No. 4, pp. 843–851, 2011.
2) Arp, H.P.H., et al.: Predicting Pore Water EPA-34 PAH Concentrations and Toxicity in Pyrogenic-Impacted Sediments Using Pyrene Content, *Environ. Sci. Technol.*, Vol. 45, No. 5139–5146, 2011.
3) Hawthorne, S.B., Miller D.J., and Kreitinger J.P.: Measurement of total polycyclic aromatic hydrocarbon concentrations in sediments and toxic units used for estimating risk to benthic invertebrates at manufactured gas plant sites, *Environ. Toxicol. Chem.*, Vol. 25, No. 1, pp. 287–296, 2006.