

# A new coherence test procedure of environmental quality objectives based on multi-media monitoring data and its application to polycyclic aromatic hydrocarbons in Korea

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## ABSTRACT

The goal of the present study was to determine if coherence was maintained among the maximum permissible concentrations (MPCs) of 15 PAHs in air, soil, water, and sediment proposed in Korea. Coherence was tested for each of the five medium pairs (soil/air, water/air, water/soil, sediment/soil, and water/sediment) using concurrently measured data of PAHs levels in those media. The coherence test was possible in the present study under the condition that the PAHs emission occurs only in air. The sources of uncertainty for assessing coherence using the monitoring data included the strength of evidence to support the assumption of near-steady state or steady state, the choice of the confidence interval, and the monitoring data set used for the test. While subject to the uncertainties, a number of the proposed MPCs of PAHs were determined not to be coherent. This work is the first one presenting a coherence test procedure based on multimedia monitoring data and the test results of coherence among the MPCs of PAHs. The results suggest that future development of methodology is warranted to ensure the coherence among the environmental quality objectives while fulfilling the desired level of protection.

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## 1. Introduction

Contamination levels of a pollutant in different environmental media can influence each other by cross-media transport of the pollutant. If such influence is strong enough between any two media, the contamination levels in the media might show a positive correlation as they could co-vary. The environmental quality objectives (EQOs) of pollutants undergoing cross-media transport need to be set often for the multiple environmental media for the management of their aggregate risk to human and/or ecological health. Typically, however, the EQOs have been independently derived for individual media [1] neglecting that the contamination levels could co-vary according to some relationships as a result of the cross-media transport. The independently derived EQOs cannot always be met simultaneously unless the relationships among the EQOs are in coherence with those of the contamination levels among the media [1,2]. Therefore, maintaining coherence is an important consideration when setting the EQOs for a chemical present in multimedia environment.

The existing test procedure of coherence between the EQOs in any two media involves the comparison of the ratio of the two EQOs

with that of the concentrations in the two media at equilibrium or steady state [1]. The equilibrium or steady state condition is necessary because the concept of coherence is valid only when a fixed relationship exists between the concentration levels in the two media. Therefore, accurate estimation of the fixed relationship (i.e., the ratio of the concentrations) at equilibrium or steady state becomes critical to the test of coherence. While the equilibrium relationships are relatively simple to calculate, the steady state relationships are typically more complex and vary with emission conditions in a given environmental setting, hence use of multimedia models was suggested for the calculation [1,3]. However, use of multimedia models was limited often by the lack of adequate information on the emission rate and mode as well as other uncertainties associated with the model prediction [1,4,5].

Multimedia monitoring data can be used for coherent test in three ways. First, identifying environmental medium pairs in which chemical equilibrium has been reached [6] is useful for the coherence test of EQOs because use of a multimedia model, which always bears burden of prediction uncertainty, can be avoided for those medium pairs [1]. Second, by comparing the model prediction with the multimedia data, the performance of multimedia models can be better assessed for improvement, hence the models can be applied more rigorously for coherence test purpose. Third, the multimedia data can be used directly for coherence test under the assumption that the concentration relationships calculated using the measured

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data represent those at equilibrium or steady state. Whether the assumption is met might be determined by assessing long term monitoring data. Also, information on the emission rate and mode may be used to assist in assessing whether the assumption is or is likely to be met. As presented in detail in [Supplementary materials](#), it is the ratios of emission rates occurring among different environmental media that change the concentration ratio at steady state between a pair of environmental media. That is, the concentration ratio at steady state could remain unchanged under the emission condition that the emission ratios are maintained constant regardless of whether the individual rates change or not. As the concentration ratios are more likely to be at steady state where the emission condition is met for a longer period, examining if the emission condition holds would be useful particularly in the absence of long term monitoring data.

Concurrent monitoring of PAHs levels in multiple environmental media has been conducted over the past few years in several areas of Korea [7]. The monitoring data have been assessed to provide the distribution and the concentration relationships of PAHs in multimedia [6] and to describe their fate and transport [8,9]. Meanwhile, the maximum permissible concentrations (MPCs) of PAHs in air, soil, water, and sediment have been proposed for human and ecological health in Korea [10]. Coherence test for the MPCs of PAHs was deemed necessary as no consideration on the correlations among the concentrations in the multimedia was given in setting the MPCs. Therefore, built partly on the previous work [6] where individual PAHs have already been identified for which the equilibrium relationships hold in various medium pairs, the monitoring data based coherent test was attempted for the first time and the results are reported in the present paper.

The goal of the present paper was to determine if coherence is maintained among the maximum permissible concentrations (MPCs) of PAHs in air, soil, water, and sediment. To fulfill the goal, this work presents (i) a monitoring data based coherence test procedure and (ii) the results of the coherence tests for the MPCs of the individual PAHs.

## 2. Materials and methods

### 2.1. Study areas

The details of the study areas and sampling locations were presented previously [6]. Briefly, three study areas (Seoul, Shihwa/Banwol, and Taegu) (Fig. 1 of Ref. [6]) were chosen to cover a range of different land cover types. Seoul is a metropolitan city (population of about 10 million in 605 km<sup>2</sup>) with little industrial activity. Taegu is a city (population of about 2.5 million in 884 km<sup>2</sup>) with moderate industrial activities (textile, mechanical and metals). The Shihwa/Banwol industrial complex (about 30 km<sup>2</sup>) was constructed over the period from 1977 to 1995 for small to middle scale manufacturing plants of diverse industries. To better represent the contamination level within each area, two sites were studied in each of the three areas, i.e., an urban (SL-U) and a suburban (SL-SU) site in Seoul, industrial sites (SI and BI) in Shihwa/Banwol, and an urban (TU) and an industrial (TI) sites in Taegu.

### 2.2. Sampling

Sampling of the four media (air: gas and particulate matters (PMs) separately, water: dissolved and suspended solids (SS) phases separately, soil, and sediment) were conducted concurrently at each site. More details of the sampling procedures, sampling periods, and number of samples were also described previously [6].

### 2.3. Chemical analysis

Chemical analysis was performed on 16 PAHs (naphthalene, acenaphthylene (AC), acenaphthene (ACE), fluorene (FL), phenanthrene (PH), anthracene (AN), fluoranthene (FLR), pyrene (PY), benzo[a]anthracene (BaA), chrysene (CH), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DA), benzo[g,h,i]perylene (BPE)) by the procedures described elsewhere [6,11]. The analytical result of naphthalene was not presented as the recovery of the surrogate standard, naphthalene-d<sub>8</sub>, did not always meet the quality control limit (40%). Additionally, environmental parameters such as PMs, SS, organic carbon (OC) content in soil, SS and sediment, and dissolved organic carbon in water (DOC) were also measured using the Korean standard methods [12].

### 2.4. Assessment of concentration relationships among environmental media

For testing coherence among EQOs based on measured concentration data, the data should be assessed to confirm that the observed concentration relationships among various media are those at equilibrium or steady state condition. Throughout the present study, the concentration relationship was denoted by the ratio of concentrations between a medium pair. The ratio is influenced by many factors including the characteristics of environmental media, physicochemical and fate properties of pollutants, meteorological factors, and emission mode (Eqs. (S1)–(S9)). Because all these factors vary with time and space, the ratio should have a range of value. The range could be statistically estimated from appropriate multimedia monitoring data as was done in a previous study [6].

#### 2.4.1. Equilibrium state

The assessment procedure for equilibrium state in the study areas was presented elsewhere [6] in detail. Briefly, the theoretical relationship of the concentration ratio that would hold at equilibrium state for each medium pair was first derived and its 95% interval was estimated using Monte Carlo calculation (5000 trials) with probability distributions of the values of individual parameters representing the temporal and spatial variability. The 95% interval of the observed concentration ratio for the same pair of media was also calculated from the multimedia monitoring data and statistically compared with that of theoretical concentration ratio. From the comparison, the PAHs that were at equilibrium state between two environmental media in the study areas were identified (i.e., AC, PH, and BaA between air and water; AC, PH, FLR, PY, BaA, CH, BbF, BkF, BaP, IP, DA, BPE between soil and sediment) [6].

#### 2.4.2. Steady state

In the present work, further identification of the PAHs was necessary of which the concentration ratio between two media was at steady state. Steady state could be observed for the concentration ratio between a medium pair in two cases, i.e. (i) where the individual concentrations in the two media stay constant and (ii) where the individual concentrations co-vary such that their ratio does not change with time. The first case was not likely in the study areas because the emission rates and the PAHs concentrations were not constant as described in more details in Section 3. Therefore, the possibility of the second case was evaluated in the present work by examining if the theoretical relationship of the concentration ratio (Eq. (S9) in [Supplementary materials](#)) under the PAH emission mode in the study areas was applicable to the present work. To further support the evaluation result, statistical tests were performed on the time change in individual PAH levels where possible

(i.e., in each of air, water, and sediment in the Seoul areas for which monitoring was conducted from 2001 to 2003, from 1999 to 2003, and from 1999 to 2004 for air, water, and sediment, respectively). Whether or not the slope of the annual geometric mean of the PAH with respect to time (year) is statistically different from zero (with 95% significance, by using SPSS v12) was determined by the test. Soil was assumed to be identical to sediment in Seoul because the concentration of PAHs in sediment was directly governed by that in soil [8,9], hence the time change of the sediment concentration would reflect that of soil. The annual geometric mean concentration values were used for the test to take into account the seasonal variations.

Shapiro–Wilk test [13] indicated that the observed concentration ratios were well described by log normal distribution. Therefore, as the range of the concentration ratios for those PAHs identified to be at steady state, the 95% confidence intervals were determined using the distributions determined from the logarithms of the observed concentration ratios.

2.5. Test of coherence

In the present work, the coherence test was conducted for five pairs of media. Three medium pairs of air–water, air–soil, and water–sediment were included because they are in direct contact with each other. The medium pair of soil–water was included as the two media are connected for chemical transport primarily by surface run-off. The pair of soil–sediment was selected because the sediment concentration was found to be strongly influenced by that in soil to establish a clear correlation of the PAH levels between the two media due to the hydrological conditions in the study areas [8].

To decide coherence, the ratio of MPCs of a medium pair was compared with the range of the observed concentration ratio of the two media. The criterion for two MPCs to be coherent should generally satisfy the following conditions:

$$C_2 \leq MPC_2 \quad \text{if } C_1 \leq MPC_1 \quad (1)$$

and

$$C_1 \leq MPC_1 \quad \text{if } C_2 \leq MPC_2 \quad (2)$$

where  $C_1$  and  $C_2$  denote the concentrations at equilibrium or steady state in media 1 and 2, respectively, and  $MPC_1$  and  $MPC_2$  denote the MPCs in media 1 and 2, respectively. The conditions (1) and (2) can be satisfied by the coherence criterion below as proposed previously [1].

$$\frac{MPC_2}{MPC_1} = \frac{C_2}{C_1} \quad (3)$$

However, where a specific emission mode is known and anticipated to be maintained, relaxation of the coherence criterion (3) could be allowed. As discussed in more details in the results and discussion section, coherence test in the present work relied mainly on the estimation that PAHs emission was almost solely from atmospheric sources. Under this emission condition, the direction of net chemical flux among some media is fixed at steady state. For example, the direction would always be from air to soil or to water at steady state. Hence the concentration change would also be propagated to the direction from air to soil or water but not to the reverse direction. The coherence criterion, therefore, is required to satisfy only the following condition;

$$C_s \leq MPC_s \quad \text{if } C_p \leq MPC_p \quad (4)$$

where subscript  $s$  and  $p$  denote secondary and primary media, respectively. Primary medium refers to the one of net chemical

Table 1 Maximum permissible concentrations for human and ecosystem health and the observed PAHs levels in the present study.

| PAHs | Air (ng/m <sup>3</sup> ) |              |         | Water (µg/L)   |              |         | Soil (ng/g)  |              |             | Sediment (ng/g) |             |         |       |
|------|--------------------------|--------------|---------|----------------|--------------|---------|--------------|--------------|-------------|-----------------|-------------|---------|-------|
|      | Human health             | Human health | Obs.    | Human health   | Human health | Obs.    | Human health | Human health | ECO. health | Human health    | ECO. health | Obs.    |       |
|      | WHO/IPCS                 | NE           | geomean | WHO/IPCS       | NE           | geomean | WHO/IPCS     | NE           | geomean     | NE              | geomean     | geomean |       |
| AC   | 2800                     | 4000         | 0.57    | 0.08           | 8.1          | 0.0006  | 248          | 8400         | 150         | 8400            | 150         | 0.75    | 5.87  |
| ACE  | 2800                     | 19,000       | 0.28    | <b>0.08</b>    | 24           | 0.0007  | 248          | 13,000       | 57          | 13,000          | 57          | 0.41    | 6.71  |
| FL   | 2800                     | 24,000       | 1.88    | <b>0.08</b>    | 31           | 0.0035  | <b>248</b>   | 240,000      | 626         | 240,000         | 626         | 1.31    | 21.2  |
| PH   | 2800                     | 20,000       | 6.79    | <b>0.08</b>    | 47           | 0.196   | <b>248</b>   | 58,000       | 846         | 58,000          | 846         | 15.98   | 41.9  |
| AN   | 2800                     | 2000         | 0.66    | <b>0.008</b>   | 3            | 0.056   | <b>248</b>   | 38,000       | 707         | 38,000          | 707         | 1.05    | 46.9  |
| FLR  | 2800                     | 22,000       | 4.21    | 0.08           | 56           | 0.0027  | <b>248</b>   | 98,000       | 1300        | 98,000          | 1300        | 25.97   | 111   |
| PY   | 2800                     | 32,000       | 3.48    | <b>0.08</b>    | 44           | 0.0023  | <b>248</b>   | 230,000      | 510         | 230,000         | 510         | 17.38   | 53    |
| BaA  | 28                       | 190          | 0.45    | 0.0008         | 0.26         | 0.0004  | <b>2.5</b>   | 6300         | 75          | 6300            | 75          | 5.46    | 31.7  |
| CH   | 280                      | 2000         | 0.97    | <b>0.008</b>   | 2.4          | 0.0007  | <b>24.8</b>  | 49,000       | 100         | 49,000          | 100         | 14.12   | 57.1  |
| BbF  | 28                       | 280          | 1.2     | <b>0.0008</b>  | 0.3          | 0.0006  | 2.5          | 7700         | -           | 7700            | -           | 18.03   | -     |
| BkF  | 28                       | 360          | 0.61    | 0.0008         | 0.26         | 0.0003  | 2.5          | 5600         | -           | 5600            | -           | 8.79    | 7.66  |
| BaP  | 2.8                      | 15           | 0.52    | <b>0.00008</b> | 0.013        | 0.0003  | <b>0.25</b>  | 370          | 211         | 370             | 211         | 6.92    | 31.9  |
| IP   | 28                       | 680          | 1.34    | 0.0008         | 0.34         | 0.0004  | 2.5          | 7900         | -           | 7900            | -           | 28.5    | 14.12 |
| DA   | 2.8                      | 30           | 0.3     | 0.00008        | 0.027        | 0.0003  | 0.25         | 730          | -           | 730             | -           | 8.09    | 4     |
| BPE  | 282                      | 9700         | 1.64    | 0.008          | 4.1          | 0.0005  | 24.8         | 440,000      | -           | 440,000         | -           | 26.68   | 15.49 |

WHO/IPCS, World Health Organization/International Programme on Chemical Safety; NE, Netherlands; ECO. health, ecosystem health; Obs. geomean, geometric mean of the observed concentrations. Notes: (1) The maximum permissible concentration (MPC) values in bold denote those selected for the coherence test where two MPVs (i.e., human and ecosystem health) are available for each PAH. (2) Two different human MPCs were determined using the methods of WHO/IPCS and Netherlands (Refs. [14,15]). (3) The underlined observed concentration values in *italics* denote those exceeding the MPCs either for human or for ecosystem health.

export and secondary medium refers to the one of net chemical import. The coherence criterion satisfying the condition (4) is:

$$\frac{MPC_s}{MPC_p} \geq \frac{C_s}{C_p} \quad (5)$$

As mentioned above, air was always primary medium between air and other medium. Soil was primary medium between the medium pair of soil–water or soil–sediment in the present work. Therefore, the criterion (5) was used for coherent test for these medium pairs. Between water and sediment, the coherence criterion (3) was used as primary medium was not clearly distinguishable.

Coherence was determined in the present work by statistically testing if the coherence criterion (3) or (5) was met. That is, the two MPCs were called coherent with each other if the ratio of the MPCs ( $MPC_s/MPC_p$ ) fell within or above the 95% interval of the observed concentration ratio (criterion (5)) for all the medium pairs except the water–sediment pair for which the MPC ratio should fall within the 95% interval (criterion (3)) to be coherent.

The coherence test procedure based on the monitoring data used in the present study is shown in Fig. 1.

Two MPCs (each for human and ecosystem) were available for individual PAHs in each of water and soil [10]. Of the two MPCs, the stricter (i.e., of the lower value) was chosen for the coherence test. Table 1 lists the final set of MPC values for individual PAHs used for the coherence test in the present study. The human MPCs used for the coherence test in the present study were originally derived using the method of World Health Organization/International Programme on Chemical Safety [14]. In the previous study [13], an additional set of human MPCs have also been derived for comparison purpose by using the method proposed in the Netherlands (Table 1) [15]. The coherence test was also conducted by using the set of the human MPCs of the Netherlands (Ne-MPCs hereafter) and the ecosystem MPCs. The MPC set for this case is also presented in Table 1.

### 3. Results and discussion

#### 3.1. Steady state

It was estimated that a predominant portion (> about 95%) of PAHs was originated from fossil fuel combustion throughout the terrestrial areas of Korea [16]. The estimation was supported by the typical indices characterizing the source types [17,18], e.g., the ratios of PH to AN, FLR to PY, BaA to CH, and IP to BPE. These indices consistently suggested that PAHs in the study areas were primarily from pyrogenic sources [9,19], indicating that PAHs were initially released into air and redistributed to other media by various cross-media processes. In this emission mode, concentration ratios at steady state is a function of the rate coefficients of intra- and inter-media processes that change only with meteorological and environmental conditions (Eq. (S9) and its derivation procedure in Supplementary materials for more details). Theoretically, therefore, the concentration ratios at steady state would remain constant within an area as long as the meteorological and environmental conditions do not change in the area. The concentration ratio between a medium pair then would always be in the course toward the same one steady state condition even if the emission rate changes, which was shown in a previous modeling study [16]. It was also shown in the study [16] that the concentration ratio between two media could be stabilized quickly while the individual concentrations are still changing. The stabilization of the concentration ratio would occur more quickly if the change in the emission rate is smaller because perturbations in the magnitude of the concentration ratio that might be introduced by changes in the emission rate would also be small. The annual fossil fuel consumption (each of coals, oils, and gases) in the study areas changed by less than ±4%

**Table 2**  
Discrepancy of the geometric means of the concentration ratios among the three study areas.

|   | AC              | ACE             | FL              | PH              | AN       | FLR             | PY              | BaA             | CH              | BbF             | BkF             | BaP             | IP              | DA              | BpE             |
|---|-----------------|-----------------|-----------------|-----------------|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Concentration ratio between water and air ( $C_{water}/C_{air}$ )           |                 |                 |                 |                 |          |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| SL-S/B  | 5.10E+00        | 7.50E+00        | 2.40E+00        | 2.00E+00        | 3.40E+00 | 1.70E+00        | 1.20E+00        | 1.30E+00        | 2.10E+00        | 1.30E+00        | 1.30E+00        | 1.30E+00        | 2.40E+00        | 2.20E+00        | 1.10E+00        |
| SL-T  | 1.50E+00        | 2.20E+00        | 1.20E+00        | 2.30E+00        | 2.50E+00 | 1.90E+00        | 1.20E+00        | 1.70E+00        | 1.10E+00        | 1.20E+00        | 1.10E+00        | 1.20E+00        | 2.30E+00        | 1.00E+00        | 3.90E+00        |
| S/B-T   | 3.50E+00        | <b>1.60E+01</b> | 2.90E+00        | 1.10E+00        | 1.40E+00 | 1.10E+00        | 1.00E+00        | 1.30E+00        | 1.80E+00        | 1.50E+00        | 1.40E+00        | 1.50E+00        | 1.00E+00        | 1.00E+00        | 3.40E+00        |
| Concentration ratio between soil and air ( $C_{soil}/C_{air}$ )             |                 |                 |                 |                 |          |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| SL-S/B  | 3.20E+00        | 2.60E+00        | 3.80E+00        | 4.50E+00        | 8.20E+00 | 7.50E+00        | 8.50E+00        | 6.80E+00        | 4.80E+00        | 6.60E+00        | 6.80E+00        | 6.60E+00        | 5.20E+00        | <b>2.00E+01</b> | 6.60E+00        |
| SL-T  | 7.80E+00        | <b>2.70E+01</b> | <b>1.30E+01</b> | 3.90E+00        | 6.60E+00 | 5.70E+00        | 6.80E+00        | 7.60E+00        | 7.50E+00        | 8.60E+00        | 7.20E+00        | 6.10E+00        | 9.50E+00        | 1.00E+00        | 6.30E+00        |
| S/B-T   | 2.40E+00        | <b>1.00E+01</b> | 3.50E+00        | 1.10E+00        | 1.20E+00 | 1.30E+00        | 1.30E+00        | 1.10E+00        | 1.60E+00        | 1.30E+00        | 1.10E+00        | 1.10E+00        | 1.80E+00        | 1.00E+00        | 1.00E+00        |
| Concentration ratio between water and soil ( $C_{water}/C_{soil}$ )         |                 |                 |                 |                 |          |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| SL-S/B  | 3.40E+00        | 3.70E+00        | 3.70E+00        | <b>1.20E+01</b> | 7.90E+00 | <b>2.00E+01</b> | <b>1.60E+01</b> | <b>1.10E+01</b> | <b>1.60E+01</b> | <b>1.40E+01</b> | <b>1.30E+01</b> | 5.00E+00        | <b>2.30E+01</b> | 9.10E+00        | <b>1.30E+01</b> |
| SL-T  | 2.00E+00        | 1.40E+00        | 3.50E+00        | 9.60E+00        | 4.60E+00 | <b>1.30E+01</b> | <b>1.10E+01</b> | 6.60E+00        | 9.60E+00        | 8.80E+00        | 9.10E+00        | 7.40E+00        | <b>4.90E+01</b> | 1.00E+00        | <b>3.00E+01</b> |
| S/B-T   | 1.70E+00        | 2.50E+00        | 1.10E+00        | 1.30E+00        | 1.70E+00 | 1.50E+00        | 1.50E+00        | 1.60E+00        | 1.60E+00        | 1.50E+00        | 1.50E+00        | 1.50E+00        | 2.10E+00        | 1.00E+00        | 2.40E+00        |
| Concentration ratio between water and soil ( $C_{sediment}/C_{soil}$ )      |                 |                 |                 |                 |          |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| SL-S/B  | 2.00E+00        | 1.30E+00        | 1.10E+00        | 2.00E+00        | 1.40E+00 | 2.00E+00        | 2.10E+00        | 1.90E+00        | 2.10E+00        | 2.50E+00        | 2.30E+00        | 1.60E+00        | 2.70E+00        | 3.00E+00        | 2.30E+00        |
| SL-T  | 1.50E+00        | 6.70E+00        | 1.10E+00        | 1.10E+00        | 1.90E+00 | 2.20E+00        | 1.90E+00        | 2.30E+00        | 2.50E+00        | 2.40E+00        | 2.80E+00        | 2.50E+00        | 2.10E+00        | 1.00E+00        | 2.70E+00        |
| S/B-T   | 3.00E+00        | 8.70E+00        | 1.00E+00        | 2.30E+00        | 2.70E+00 | 4.40E+00        | 4.00E+00        | 4.30E+00        | 5.40E+00        | 6.10E+00        | 6.50E+00        | 4.10E+00        | 5.70E+00        | 1.00E+00        | 6.20E+00        |
| Concentration ratio between sediment and water ( $C_{sediment}/C_{water}$ ) |                 |                 |                 |                 |          |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| SL-S/B  | <b>2.00E+01</b> | <b>2.20E+01</b> | 6.40E+00        | 5.90E+00        | 2.40E+00 | 6.40E+00        | 5.90E+00        | 3.80E+00        | 4.90E+00        | 3.40E+00        | 5.20E+00        | 5.60E+00        | 8.50E+00        | 2.70E+00        | 4.40E+00        |
| SL-T  | <b>2.70E+01</b> | 1.10E+00        | 5.30E+00        | 9.70E+00        | 4.70E+00 | <b>1.60E+01</b> | <b>1.20E+01</b> | 8.40E+00        | <b>1.30E+01</b> | 9.80E+00        | <b>1.60E+01</b> | <b>2.40E+01</b> | <b>1.20E+02</b> | 1.00E+00        | <b>9.30E+01</b> |
| S/B-T   | 1.40E+00        | <b>2.40E+01</b> | 1.20E+00        | 1.60E+00        | 2.00E+00 | 2.40E+00        | 2.00E+00        | 2.20E+00        | 2.70E+00        | 2.90E+00        | 3.10E+00        | 4.30E+00        | <b>1.40E+01</b> | 1.00E+00        | <b>2.10E+01</b> |

SL: Seoul, S/B: Shihwa/Banwol, T: Taegue.

Notes: (1) The discrepancy in the table is the ratio of the greater geometric mean to the smaller one of the two areas compared. (2) The discrepancy greater than a factor of 10 is shown in bold.



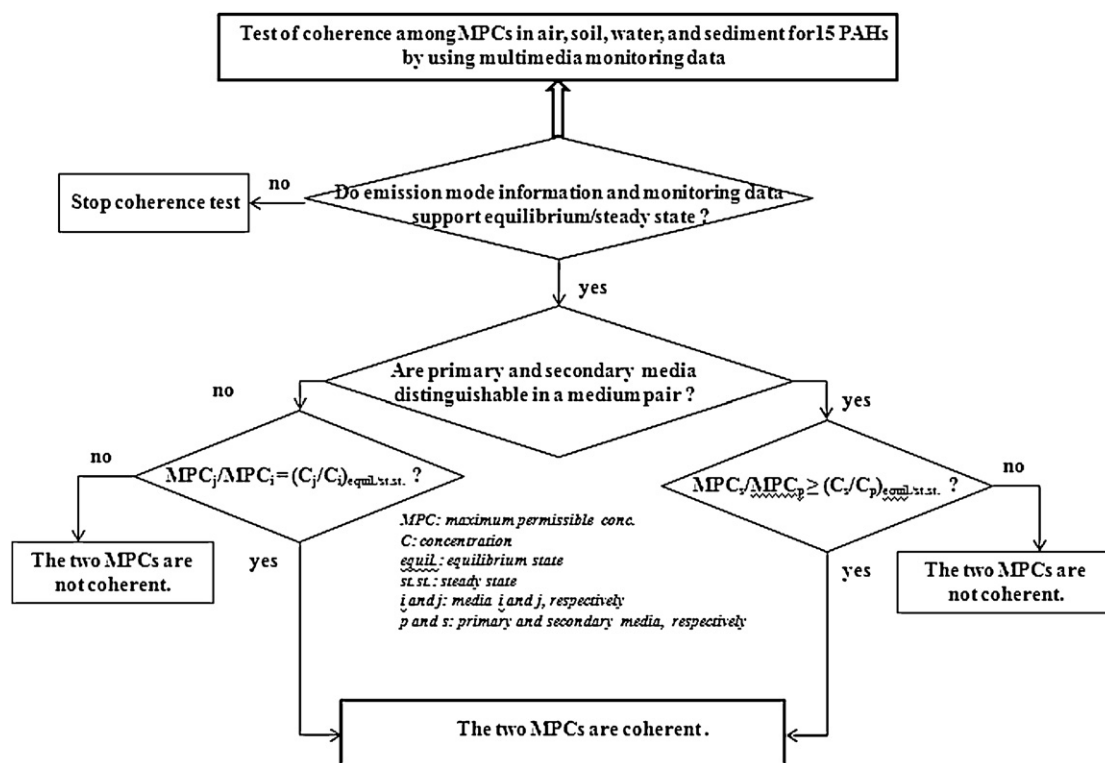


Fig. 1. The monitoring data based coherence test procedure used in the present study.

from 1999 to 2009 [20], strongly indicating no sudden change in the atmospheric PAH emission rates over the period. The emission conditions (i.e., mainly atmospheric emission and with no sudden change in the rate) suggested a possibility that the ratios of the concentrations were likely at or near steady state in the study areas while the concentrations in individual media might be transient.

It is also expected from Eq. (S9) in Supplementary materials that the concentration ratios of PAHs at steady state in different areas would be similar if the meteorological and environmental conditions in the areas are similar. Therefore, discrepancies in the concentration ratios among the areas would become smaller as the concentration ratio approaches closer to steady state in each of the areas. The geometric means of the observed concentration ratios differed by less than a factor of 10 for most cases (Table 2) among the three study areas where their meteorological and environmental conditions are not substantially different (Table S1), supporting that the concentration ratios might be at or near steady state in the three areas.

Statistical tests were conducted to assess if the concentration levels in individual media has been significantly changing. Table 3 summarizes the results of the statistical tests on the time change in individual PAH levels in the three media in Seoul. The slopes of all the 15 PAHs in air, sediment, and water were not significantly different from zero except seven PAHs (ACE, FL, PH, PY, FLR, BaP, and BPE) in water. The slopes for these seven PAHs ranged typically from 10%/year to 50%/year.

All the PAHs in soil were also assumed to have the slopes that are not significantly different from zero as the time change of the sediment concentration reflected that of soil. The assumption was statistically examined by pooling the soil concentration data in the present work and those previously reported [7] for 1999 and 2000 in a commercial and residential area (Shinchon) near the study areas of Seoul. The land use type, hence the emission characteristics of this area were considered to be similar to those of the SL-U site in the present study, which was supported by the statistical

assessment that the PAHs levels in this area were not significantly ( $p > 0.05$ ) different from those in the SL-U site. The statistical test showed that all the PAHs but three (PY, BaA, and BaP) were of the slopes that are not significantly different from zero (Table 3), indicating that the zero slope assumption for soil was reasonable for Seoul.

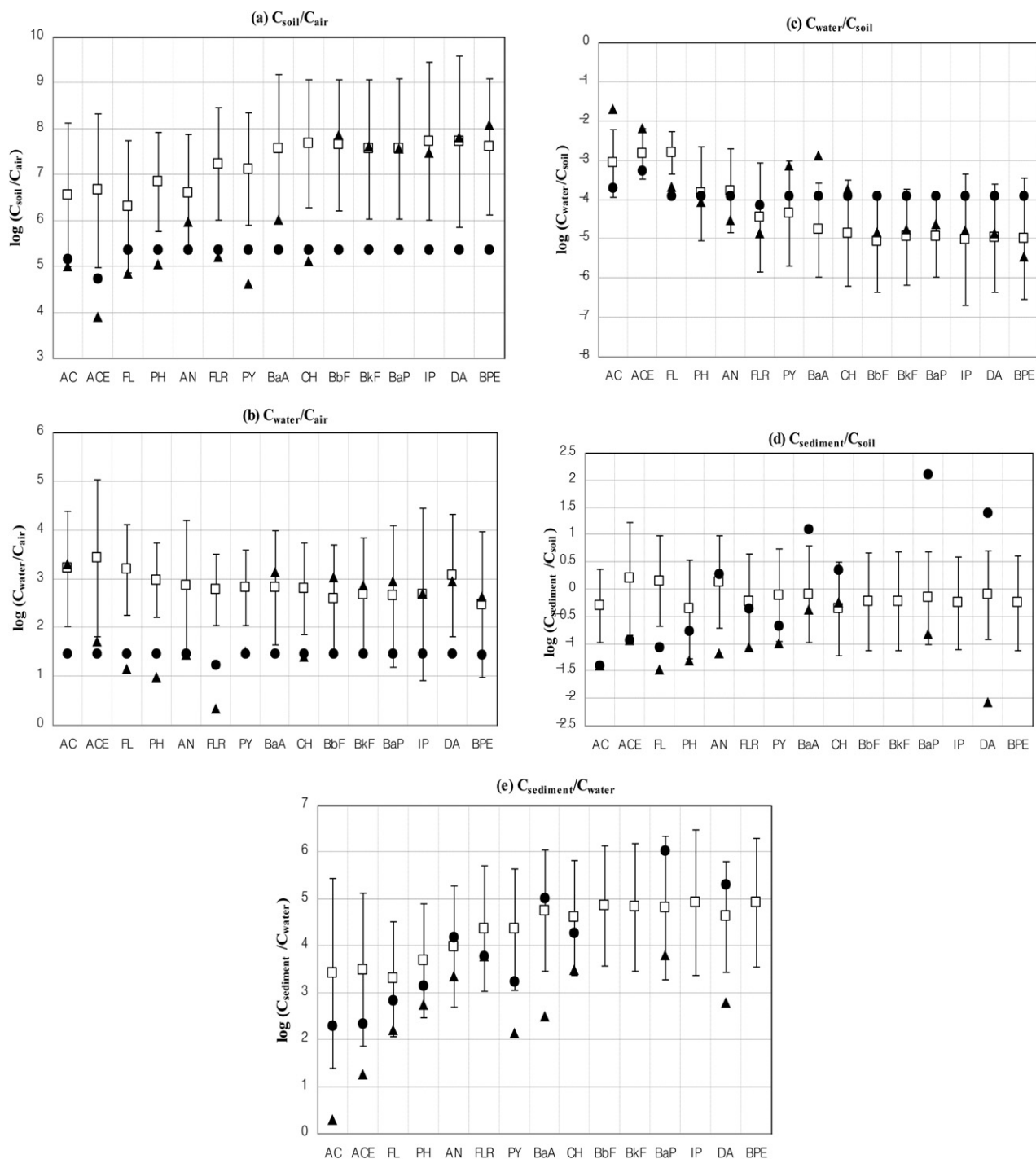
All the statistical test results indicated that most of the PAHs levels in individual media did not significantly change with time. The results were consistent with that there has been no sudden change in the emission rate and also supported that the study areas could be at or near steady state in terms of the PAHs concentration ratios.

Combining the theoretical relationship of the concentration ratio with the emission mode and its estimated rate for the study areas, and the statistical results on the time change in the PAHs levels, the study areas were viewed in the present work as an environmental system where the ratios of the PAHs concentrations were at or near steady state while the individual concentrations might be changing with time.

### 3.2. Coherence of MPCs

#### 3.2.1. Soil/Air

As shown in Fig. 2a, the ratio of MPCs of soil to those of air ( $MPC_{soil}/MPC_{air}$ ) are out of the 95% interval for all PAHs but AC, FL, and AN. All the MPCs ratios out of the interval were smaller than the lower bound (2.5 percentile) of the observed concentration ratios ( $C_{soil}/C_{air}$ ), indicating that the two MPCs cannot always be met simultaneously. As listed in Table 1, the observed levels of heavy PAHs (from BaA to BPE) in soil (geometric means) exceeded their  $MPC_{soil}$  although the observed atmospheric levels (geometric mean) met their  $MPC_{air}$ . The values of  $MPC_{soil}/MPC_{air}$  deviated from the lower bound of  $C_{soil}/C_{air}$  by a factor of 10 or less, both the MPCs could be met simultaneously only when the atmospheric level of PAHs is lower than  $MPC_{air}$  by a factor of about 10 or more,



**Fig. 2.** Coherence of the MPCs of PAHs between (a) soil and air, (b) water and air, (c) water and soil, (d) sediment and soil, and (e) sediment and water. Open square and error bar: geometric mean and the 95% interval of the ratio of the observed concentrations, respectively, closed circle: ratio of MPCs from the set of WHO/IPCS MPCs and ecosystem MPCs, closed triangle: ratio of MPCs from the set of Ne-MPCs and ecosystem MPCs.

which was the case for PAHs from AC to PY (Table 1). Comparatively, AN, BaA, and the heavy PAHs from BbF to BPE appeared coherent when the Ne-MPCs were used because the Ne-MPCs of soil are greater than the MPCs of WHO/IPCS for those PAHs.

### 3.2.2. Water/Air

The MPCs of water and air are not coherent for all the tested PAHs (Fig. 2b) except BaP, IP, and BPE. For those that are not coherent, the ratios of MPCs ( $MPC_{water}/MPC_{air}$ ) were below the lower bound (2.5 percentile) of the interval of the observed concentration

ratios ( $C_{water}/C_{air}$ ) by a factor of 10 or less. Therefore, the PAHs concentration in water could exceed the  $MPC_{water}$  even though the  $MPC_{air}$  is met. For instance, the concentration of DA in water exceeded the  $MPC_{water}$  while the  $MPC_{air}$  was met (Table 1). Again, for the  $MPC_{water}$  and  $MPC_{air}$  that are not coherent with each other could simultaneously be met only if the atmospheric concentration of the PAHs is kept lower than their  $MPC_{air}$  by 10 or more.

When use of the Ne-MPCs for human health or the MPCs for ecosystem was considered for coherence test, the MPCs for ecosystem health were selected for all PAHs but BbF as they are stricter

**Table 3**  
The *p*-values of the statistical test for the slope of the PAH levels with respect to time.

| Medium   | Sampling site I.D. | Monitoring period | AC    | ACE          | FL           | PH           | AN    | FLR          | PY           | BaA          | CH    | BbF   | BkF   | BaP          | IP    | DA    | BPE          |
|----------|--------------------|-------------------|-------|--------------|--------------|--------------|-------|--------------|--------------|--------------|-------|-------|-------|--------------|-------|-------|--------------|
| Air      | SL-SU              | 2001–2003         | 0.431 | 0.308        | 0.268        | 0.476        | 0.462 | 0.641        | 0.521        | 0.542        | 0.438 | 0.365 | 0.197 | 0.415        | 0.892 | 0.306 | 0.875        |
| Water    | SL-SU              | 1999–2003         | 0.61  | 0.35         | 0.09         | <b>0.027</b> | 0.135 | <b>0.045</b> | <b>0.045</b> | 0.159        | 0.407 | 0.065 | 0.882 | <b>0.018</b> | 0.265 | 0.752 | <b>0.017</b> |
|          | SL-U               | 1999–2004         | 0.248 | <b>0.048</b> | <b>0.027</b> | <b>0.011</b> | 0.131 | 0.054        | <b>0.02</b>  | 0.906        | 0.071 | 0.881 | 0.321 | 0.736        | 0.127 | 0.73  | 0.547        |
| Sediment | SL-SU              | 1999–2003         | 0.159 | 0.298        | 0.062        | 0.272        | 0.26  | 0.455        | 0.083        | 0.556        | 0.956 | 0.353 | 0.554 | 0.199        | 0.943 | 0.821 | 0.5          |
|          | SL-U               | 1999–2004         | 0.859 | 0.291        | 0.973        | 0.461        | 0.274 | 0.195        | 0.403        | 0.145        | 0.369 | 0.424 | 0.062 | 0.484        | 0.946 | 0.977 | 0.943        |
| Soil     | SL-U               | 1999–2003         | 0.272 | 0.585        | 0.801        | 0.818        | –     | 0.26         | <b>0.02</b>  | <b>0.025</b> | 0.176 | 0.367 | 0.095 | <b>0.033</b> | 0.43  | –     | 0.223        |

Notes: (1) SL-SU and SL-U denote the suburban and urban sites in Seoul, respectively. (2) The *p*-values smaller than 0.05 are shown in bold and italic to denote the cases where the slopes are statistically not zero. (3) The test result for soil was obtained by pooling the data of the present study and an independent monitoring data set for an urban site (Shinchon) for the years 1999 and 2000.

than the Ne-MPCs. Nonetheless, the selected MPCs for ecosystem health are greater than those of WHO/IPCS by at least several times. As the result, MPC<sub>water</sub> and MPC<sub>air</sub> are coherent for AC and heavy PAHs (BaA, BbF, BkF, BaP, IP, DA, and BPE).

### 3.2.3. Water/Soil

As shown in Fig. 2c, the MPCs of water and soil are coherent for all the PAHs except FL.

With the Ne-MPCs and MPCs for ecosystem health, FL was the only PAH that is not coherent. Although the ratios of MPC<sub>water</sub> to MPC<sub>soil</sub> for AC and BaA are out of the 95% range of the observed concentration ratio ( $C_{\text{water}}/C_{\text{soil}}$ ), they were determined to be coherent as the ratios of the MPCs for these PAHs were greater than the upper bound (97.5 percentile).

### 3.2.4. Sediment/Soil

It was found previously [8] that the contamination of sediment with PAHs was directly influenced by that of soil in the study areas. Because the levels of PAHs in the two media would strongly co-vary, keeping the MPCs between the two media coherent is particularly important. As shown in Fig. 2d, the MPCs are not coherent for three PAHs (i.e., AC, ACE, and FL) for which the MPC ratios fell below the lower bounds of the intervals. Although not coherent, AC, ACE, and FL did not exceed their MPC<sub>sediment</sub> because  $C_{\text{soil}}$  was substantially lower than the MPC<sub>soil</sub> (based on the geometric means in Table 1).

The MPCs in soil for ecosystem health are lower than the Ne-MPCs for all PAHs and the MPCs in sediment were proposed only for ecosystem health. Therefore, for the coherence test between soil and sediment, only MPCs for ecosystem health were chosen for both the media. As shown in Fig. 2d, the MPCs ratios are not within the 95% interval for a total of eight PAHs (DA and six PAHs from AC to PY except FLR). The ratios of MPCs ( $\text{MPC}_{\text{sediment}}/\text{MPC}_{\text{soil}}$ ) for these PAHs were smaller than the lower bounds (2.5 percentile) of the intervals, indicating that the protection levels targeted by the MPCs<sub>sediment</sub> for the ecosystems in sediment could fail if  $C_{\text{soil}}$  approaches to MPCs<sub>soil</sub>, for example, within a factor of about 100 with DA or within a factor of two or three with ACE, FL, and AN.

### 3.2.5. Sediment/Water

Chemical potential of PAHs appeared greater in sediment than in water in the study areas [6], suggesting a net diffusive flux from sediment to water. PAHs would also be exchanged between the two media due to the actions of non-diffusive processes such as sedimentation and re-suspension of solid bound PAHs. Because the direction of net chemical transport could not be determined in the study areas, the coherence criterion (3) was used in the present work. As shown in Fig. 2e, the ratios of MPCs ( $\text{MPC}_{\text{sediment}}/\text{MPC}_{\text{water}}$ ) fall within the 95% ranges for all the PAHs for which the MPCs of both the media have been proposed (BbF, BkF, IP, and BPE: no sediment MPCs proposed), showing that the MPCs of sediment and water are coherent.

With the Ne-MPCs, MPC<sub>water</sub> and MPC<sub>sediment</sub> are coherent for FL, PH, AN, CH, FLR, and BaP (BbF, BkF, IP, and BPE: no sediment MPCs proposed). For the PAHs that are not coherent, the ratios of MPCs ( $\text{MPC}_{\text{sediment}}/\text{MPC}_{\text{water}}$ ) were smaller than the lower bound (2.5 percentile) of the intervals by less than a factor of 10. Therefore, the two MPCs could not be met simultaneously if either  $C_{\text{sediment}}$  or  $C_{\text{water}}$  is at a level within a factor less than 10 from the MPC.

It should be emphasized that the coherence test results in the present study hold under the condition that the PAHs emission occurs only in air. Various sources of uncertainty were recognized when assessing coherence using the monitoring data. Notably, the strength of evidence for the assumption of near-steady or steady state might not be unequivocal. Also, some MPC ratios that were determined not to be coherent fell very close to the bounds of the 95% intervals. This suggests that the coherence test results may

differ if intervals of different confidence level are used or if the observed data set for the test is revised by additional monitoring in time and/or space. While subject to these uncertainties, a number of the proposed Korean MPCs were found not to be coherent. The finding demonstrates a need of new EQO setting methodologies that could ensure not only the desired protection level but the coherence among the EQOs.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.12.070.

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