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KINETIC ANALYSIS: BENZO(a)PYRENE IN SOUTHEASTERN OHIO

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Abstract. Kinetic Analysis has been successful for metallic elements in relatively isolated areas. In this study it is applied to a complex organic compound in a geographical area with a large urban component. Ten media compartments are included, with man as the ultimate receptor. Field data were collected for only 6 of the media and were not used in the analysis but were compared to the calculated steady state concentrations. The greatest differences between calculated and observed values were 4.8-fold for soil and 5.4-fold for sediment. The field sampling regime for soils was biased towards areas of industrialization and probably explains the higher observed value. The lower observed value for sediment is likely due to unknown variables necessary for the estimation of the compartment size and/or the associated transfer rate constants. This study indicated that the Kinetic Analysis technique can be applied successfully to the pre-sampling estimation of the distribution of organic pollutants in environmental systems.

1. Introduction

Kinetic Analysis of environmental systems has been applied to the pathway analysis of mercury (Barry, 1979; Miller and Buchanan, 1979), lead (Wiersma, 1979, 1980) and copper (Wiersma, 1981). For these inorganic systems this type of analysis has been a successful aid in the development of sampling protocols and in the description of chemical concentration levels within environmental compartments.

Of interest to the present work is the applicability of kinetic analysis to the transport of organic compounds between environmental compartments. Chosen for this study was benzo(a)pyrene (BaP) because of its environmental significance and the wealth of data published with respect to this compound. The geographical area chosen was a portion of southeast Ohio, northern Kentucky, and western West Virginia (SEOSA). The area includes a sizable urban component which is of interest in this study.

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by plant roots into the vegetation compartments; reintraintment back into the air compartment by ground level air currents; percolation through soil into ground water; and transfer to animals during grazing.

Most of the BaP in the surface water compartment either flows out of the area or is adsorbed onto sediment. In this study suspended sediment is considered part of the surface compartment. Some of the BaP in surface water is taken up by fish while some may be transferred to animals that consume surface water. When surface water flows into the ground water aquifer, dissolved BaP is carried with it.

BaP in the sediment compartment is involved in a cycle of loss and gain by suspension into the surface water compartment and deposition from the water system. BaP is also removed from the sediment due to microbial decomposition. A small amount of BaP is transferred to bottom-feeding fish as sediment travels through their gastrointestinal tract.

The BaP in the fish compartment is either metabolized within the fish or excreted unchanged and transferred to sediment. A transfer also occurs when the fish die and decompose in the sediment.

From the vegetation compartment, BaP is transferred to soil in the form of decaying vegetation. Some BaP moves into the animal compartment as animals consume vegetation. BaP is also removed from vegetation through metabolism.

Transfers from the edible vegetation compartment are similar to those in the vegetation compartment. A portion of the edible vegetation is consumed by man resulting in an additional transfer from this compartment.

From the animal compartment, BaP will most likely be metabolized or excreted unchanged and transferred to soil. It can also be transferred to man during consumption of foodstuffs produced in the area.

Some BaP in the ground water compartment can be transferred to animals and man during consumption of water from wells, and some is transferred to vegetation by the uptake of water by plant roots. A balance exists between ground water and surface water in which the direction of water flow is toward the most depleted compartment. In general, rainfall causes a flow into the ground water compartment and the water is eventually transferred back to the surface, resulting in some transfer of BaP from ground water to surface water. A transfer also occurs during industrial pumping which transfers ground water to surface water. In addition, BaP is destroyed as ground water is treated for public use.

In the man compartment, the only transfers considered for this study are those of metabolism and the excretion of unchanged BaP. This analysis underestimates the steady state concentration of BaP in the man compartment because exposure due to personal life style (smoking, etc.) is not considered. Emphasis has been placed on environmental BaP exposure from sources external to individual human activity.

3. Description of the Compartment Sizes

The study area (SEOSA) is shown in Figure 2. Within the SEOSA there are three major urban areas, Huntington, West Virginia; Ashland, Kentucky; and Ironton, Ohio, all located along the Ohio River. Based on recent U.S. Geological Survey topographic maps (USDI, 1972) the total surface area is 525 km².

The air compartment consists of all the air located within the perimeter of the study area up to a height equal to the mean seasonal morning/afternoon NOP mixing height. The NOP mixing height value is a meteorological parameter which excludes

Fig. 2. Southeast Ohio Study Area (SEOSA) with soil and vegetation sampling Sites.

data affected by precipitation or temperature changes. The volume of the air compartment was calculated by multiplying the total surface area by the mixing height of 927 m (U.S. Department of Commerce, 1967), resulting in $4.9 \times 10^{11} \text{ m}^3$.

The soil compartment was assumed to consist of the uppermost 5 cm of soil surface in the study area except for those areas occupied by surface water and hard surfaces. This depth was chosen in order to be consistent with the sampling depth used to obtain field data. The area of surface water was estimated to be 31 km (USDI, 1972) and that of hard surfaces to be 53 km² (USDI, 1976). The bulk density of soil in the SEOSA was reported to be 1.3 g cc^{-1} (Lawrence County Ohio SGS, 1981). The mass of the soil compartment obtained was $2.9 \times 10^{10} \text{ kg}$.

The surface water compartment is made up of the section of the Ohio River and its major tributary located within the study area. The surface area of this compartment, used for total areas calculations, was based on estimates for the Ohio and Big Sandy rivers only because the surface areas of the minor tributaries was considered negligible. The volume of the surface water compartment was based on the estimated volume of the Ohio River only. The average flow rate of the Ohio River in this area is $2.1 \times 10^6 \text{ l s}^{-1}$ (ORSANCO, 1978) which is equal to $1.8 \times 10^{11} \text{ Ld}^{-1}$. Since this is the amount of surface water which is exposed to desposition, a surface volume of $1.8 \times 10^{11} \text{ l}$ was used.

The sediment compartment usually consists of all bottom sediment located in all of the rivers and tributaries within a study area. For this study however, the mass of the sediment compartment was calculated based on the following assumptions: (1) The mass of sediment in the tributaries is negligible compared to the mass of sediment of the Ohio River, and (2) in the Ohio River, sediment is found only at the edges of the river extending 6 m from each shore with an initial depth of 0.75 m decreasing to zero meters at the distance of 6 m. The density of the sediment has been reported to be 2.5 g cc^{-3} (U.S. Army Corps Engineers, 1981). Based on these figures the mass of the sediment compartment was estimated to be $5 \times 10^8 \text{ kg}$.

The vegetation compartment consists of all foliage on trees and shrubbery within the study area, but also includes grass canopies and agricultural crops. The mass of the vegetation compartment was calculated by obtaining an estimate of the surface area covered by vegetation and multiplying this area by an estimate of the overall vegetation density. The surface area of vegetative cover was tabulated from land use data obtained through aerial photography (USDI, 1976). The land use categories included were agricultural land, range land, forest land, and forested wetland. The density of the vegetation has been estimated to be $3.6 \times 10^5 \text{ kg km}^2$ (Wiersma, 1979). Based on a surface area estimate of 346 km², the mass of the vegetation compartment was calculated to be $1.2 \times 10^8 \text{ kg}$.

The edible vegetation compartment consists of vegetables grown within the study area that are consumed by man within the study area. Only the portion of the plants actually consumed are included in this compartment; the plants parts on which the vegetables grow are not included. The compartment size is based on a national per capita consumption rate of 20.4 kg/person/yr for home garden produce (Nacional

Economics Div., 1981, and U.S. Department of Commerce, 1980). For a population of 148 000 within the study area the mass of the edible vegetation compartment was calculated to be 3.0×10^6 kg.

The fish compartment is made up of all fish existing within the surface water compartment. The size of this compartment was based on fish population counts reported by ORSANCO (1977), and was estimated to be 3.5×10^5 kg.

The animal compartment consists of livestock raised within the study area. The mass of this compartment is based on an estimated 1100 dairy cows weighing 500 kg/cow, 1500 beef cattle weighing 500 kg/head, and 900 000 chickens weighing 2.2 kg/chicken (County Extension Services, 1981, and Altman and Dittmer, 1972). The mass of the animal compartment was calculated to be 3.3×10^6 kg.

The ground water compartment consists of the area's predominant aquifer which is located beneath the flood plain along the Ohio River. The amount of ground water in other areas within the study area is considered to be negligible. The size of the ground water compartment is based on an inverted triangular cross sectional shape with a maximum depth of 33 m (U.S. Army Corps Engineers, 1981). The width of the triangle was taken as the width of the floodplain at each mile mark of the river. The volume of the aquifer was calculated and was multiplied by a permeation factor (U.S. Army Corps Engineers, 1981) to give a volume for the ground water compartment of 2.7×10^{11} l.

The man compartment is made up of the total population living within the study area. The mass of the man compartment was calculated by multiplying the population of 148 000 by an average weight/person of 68 kg, giving 1.0×10^7 kg.

A summary of compartmental masses and volumes is presented in Table I.

TABLE I
Calculated compartment sizes

Air	4.9×10^{11} m ³
Soil	1.8×10^{10} kg
Surface water	1.8×10^{11} l
Sediment	5.0×10^8 kg
Vegetation	1×2^{108} kg
Edible vegetation	3.0×10^6 kg
Fish	3.5×10^5 kg
Animals	3.3×10^6 kg
Ground water	2.7×10^{11} l
Man	1.0×10^8 kg

4. Description of the Transfer Constants

4.1. k_1 AIR TO MAN

This transfer occurs through inhalation of ambient air. Based on data presented by Altman and Dittmer (1972), an average respiration rate of $17 \text{ m}^3 \text{ day}^{-1}$ is estimated for man. Wynder and Hoffman (1964), from research on the retention of BaP from

cigarette smoke, estimated of 75% retention by the lung. For a population of 148 000 the transfer constant was calculated as follows:

$$k_1 = [(0.75 \text{ retained}) \times (17 \text{ m}^3 \text{ d}^{-1} \text{ person}^{-1}) \times (148\,000 \text{ persons})] / 5.1 \times 10^{12} \text{ m}^3$$

$$k = 3.8 \times 10^{-6} \text{ d}^{-1}.$$

4.2. k_2 AIR TO SOIL

This transfer occurs during particle fallout either directly onto soil or indirectly to soil after impinging on vegetative surface. The amount of BaP which impinges upon and adheres to vegetative surfaces is not included in this calculation, but is dealt with in k_4 and k_5 , air to vegetation. Particle sizes generally associated with BaP have a representative deposition velocity of 0.4 cm s^{-1} (Sheih *et al.*, 1979). The surface area available for deposition to soil is the total area minus the areas of surface water and hard surfaces. For a mixing height of 927 m the air to soil deposition rate was calculated as follows:

$$\text{dep. vel.} = (0.4 \text{ cm s}^{-1}) (1 \text{ km}/10^5 \text{ cm}) (86400 \text{ s/d}) = 0.35 \text{ km d}^{-1}$$

$$k_2 = (0.35 \text{ km d}^{-1} / 0.927 \text{ km}) \times (451 \text{ km}^2 / 525 \text{ km}^2)$$

$$k_2 = 0.031 \text{ d}^{-1}$$

4.3. k_3 SOIL TO AIR

This type of transfer occurs when particles of BaP that have been deposited on soil are re-entrained into the air compartment by air currents. The transfer is low since the re-entrained BaP does not travel back to the original mixing height, does not travel laterally a great distance to be uniformly available to all surfaces, and is quantitatively small compared to the total BaP. A value of 10^{-5} d^{-1} was assigned to this transfer constant.

$$k_3 = 1.0 \times 10^{-5} \text{ d}^{-1}.$$

4.4. k_4 AIR TO VEGETATION

This transfer occurs when impinging particles remain on vegetative surfaces. Research indicates that most particulates accumulate in the mid-vein, center portion of leaves; some accumulation occurs in the stomates of lower leaf surfaces (Smith, 1977). For the purpose of this study it is assumed that 5% of the leaf surface retains BaP particulates, allowing for washoff and reentrainment from the remainder of the leaf. The transfer rate was calculated assuming a surface area to mass ratio for vegetation of $3.0 \text{ m}^2 \text{ kg}^{-1}$.

$$k_4 = \frac{(0.35 \text{ km d}^{-1}) [(3.0 \text{ m}^2 \text{ kg}^{-1}) (1.2 \times 10^8 \text{ kg}) (0.05)] (1 \text{ km}^2 / 10^6 \text{ m}^2)}{490 \text{ km}^2}$$

$$k_4 = 1.3 \times 10^{-2}.$$

4.5. k_5 AIR TO EDIBLE VEGETATION

This transfer occurs in the same manner as the air to vegetation (k_4) but a smaller surface area to mass ratio of $1.0 \text{ m}^2 \text{ kg}^{-1}$ is assumed, because usually not all the plant is consumed.

$$k_5 = \frac{(0.35 \text{ km d}^{-1}) [(3.0 \times 10^{-6} \text{ km}^2 \text{ kg}^{-1}) (3.0 \times 10^6 \text{ kg}) (0.05)]}{490 \text{ km}^3}$$

$$k_5 = 3.2 \times 10^{-4} \text{ d}^{-1}.$$

4.6. k_6 AIR TO SURFACE WATER

The transfer from air to surface water occurs in two ways; direct deposition onto the surface of the water, and deposition onto hard surfaces followed by runoff into surface water. This analysis assumes 100% runoff of BaP from hard surfaces. As in the other calculations involving deposition, the transfer constant is based on surface area available.

$$k_6 = \frac{(0.35 \text{ km d}^{-1}) (21 \text{ km}^2 + 53 \text{ km}^2)}{490 \text{ km}^3}$$

$$k_6 = 5.3 \times 10^{-2} \text{ d}^{-1}$$

4.7. k_7 AIR OUT

BaP is lost from the air compartment by photodegradation. Mass transfer out of the air compartment due to meteorological events is incorporated into the calculation of source strength. Work done by Korfmacher *et al.* (1980) showed that a 16% reduction of BaP adsorbed on fly ash will occur during the time it takes for deposition. The 16% reduction will actually occur in less time and then stops although the particle is still exposed to light. Although the actual photolysis rate is greater than the transfer rate used, a higher rate constant would greatly overestimate the BaP loss. Due to the difficulty in handling this rate, the photodegradation and mass transfer out of this compartment are incorporated into the calculation of the source strength. Thus,

$$k_7 = 0.$$

4.8. k_8 SOIL OUT

This transfer occurs through the microbial degradation of BaP. Lu *et al.* (1977) examined BaP degradation due to microbial activity. A plot of the values of the natural logarithm of BaP concentration (%) in soil versus time (weeks) yields a slope of 0.0069 and an intercept of 4.55 upon linear regression analysis. Therefore, the transfer rate was calculated as follows:

$$\ln[50] = 0.0069 t_{1/2} + 4.55$$

$$t \quad 92.5 \text{ weeks} = 647 \text{ d}$$

$$k_8 \quad 0.693/647 \text{ d}$$

$$k_8 \quad 0.001 \text{ d}^{-1}.$$

4.9. k_9 SOIL TO SURFACE WATER

The transfer from soil to surface water occurs during soil runoff into surface water. The Lawrence County Soil Conservation Service (1981) estimates an average $1 \times 10^6 \text{ kg/km}^2/\text{yr}$ of soil runoff into surface water. The surface area involved is the total surface area minus those for surface water and hard surfaces. The mass of the soil compartment is $2.9 \times 10^{10} \text{ kg}$ (Table I). The rate constant was calculated as follows:

$$k_9 = (2.7 \times 10^3 \text{ kg km}^{-2} \text{ d}^{-1} \times 451 \text{ km}^2) / 2.9 \times 10^{10} \text{ kg}$$

$$k_9 = 4.2 \times 10^{-5} \text{ d}^{-1}.$$

4.10. k_{10} SOIL TO EDIBLE VEGETATION

This transfer occurs through uptake of BaP from soil by the root system of the plants. The calculation of the rate constant was based on a study by Dorr and Kick (1970) who measured BaP in plants grown in soil prepared at a concentration of 3.33 ppm BaP. Their study showed an uptake of $0.15 \mu\text{g g}^{-1}$ dry weight after thirty days of growth. Assuming a 20% average dry weight for the vegetation, the transfer constant was calculated as follows:

$$k_{10} = \frac{(0.15 \mu\text{g g}^{-1}) (0.2 \text{ g g}^{-1}) (3.0 \times 10^6 \text{ kg}) / 30 \text{ d}}{(1000 \gamma / 300 \text{ g}) (2.9 \times 10^{10} \text{ kg})}$$

$$k_{10} = 3.1 \times 10^{-8} \text{ d}^{-1}.$$

4.11. k_{11} EDIBLE VEGETATION TO SOIL

This transfer would occur when unharvested edible vegetation decomposes and returns to soil. Since the edible vegetation compartment was defined by the amount of vegetation actually consumed, none is returned to soil. The transfer constant is therefore set at zero.

$$k_{11} = 0$$

4.12. k_{12} SOIL TO VEGETATION

This transfer takes place in the same manner as soil to edible vegetation (k_{10}). It was calculated similarly as follows:

$$k_{12} = \frac{(0.15 \gamma \text{ g}^{-1}) (0.2 \text{ g g}^{-1}) (1.2 \times 10^8 \text{ kg}) / 30 \text{ d}}{(1000 \mu\text{g} / 300 \text{ g}) (2.9 \times 10^{10} \text{ kg})}$$

$$k_{12} = 1.2 \times 10^{-6} \text{ d}^{-1}.$$

4.13. k_{13} VEGETATION TO SOIL

This transfer occurs during the annual decay and decomposition of vegetation. For the rate constant calculation it is assumed that 90% of the vegetation not consumed by animals returns to soil each year. The amount of vegetation consumed by animals (see k_{34}) is approximately $6.6 \times 10^6 \text{ kg yr}^{-1}$. The rate constant was calculated as follows:

$$k_{13} = \frac{(.90)(1.2 \times 10^8 \text{ kg} - 6.6 \times 10^6 \text{ kg})/365 \text{ d}}{1.2 \times 10^8 \text{ kg}}$$

$$k_{13} = 2.3 \times 10^{-3} \text{ d}^{-1}.$$

4.14. k_{14} SURFACE WATER OUT

Mass transport out of the area by the Ohio River is the dominant mechanism of BaP removal from surface water. However, there is also a simultaneous mass transport by the river into the area. The transfer constant therefore is adjusted to include movement of BaP into the area from upstream sources and is directly related to the flow rate. The concentration of BaP, (C), in incoming water is assumed to be 80% of that of outgoing water.

The transfer constant was calculated as follows:

$$(2.1 \times 10^6 \text{ l sec}^{-1}) (3600 \text{ s/hr}) (24 \text{ hr/d}) = 1.8 \times 10^{11} \text{ d}^{-1}$$

$$k_{14} = \frac{(1.8 \times 10^{11} \text{ l d}^{-1}) C - (1.8 \times 10^{11} \text{ l d}^{-1}) .80 C}{(1.8 \times 10^{11} \text{ l}) C}$$

$$k_{14} = 0.20 \text{ d}^{-1}.$$

4.15. k_{15} SURFACE WATER TO GROUND WATER

Transfers from surface water to ground water occur when water is pumped out of the ground and surface water percolates into the resulting void space. However, only the BaP dissolved in the surface water can move into the void space whereas the BaP adsorbed on particulate matter cannot. Based on data presented by Lewis (1975) for the River Trent the ratio of adsorbed BaP to dissolved BaP was approximately 77 to one. The amount of ground water pumped in the area for personal use is approximately 291 l/person/day (Mason, 1978), and that for industrial use is 1.5 times that amount (ORSANCO, 1981). The transfer rate was calculate as follows:

$$\text{Public use: } 291 \text{ l person}^{-1} \text{ d}^{-1} (148\,000 \text{ persons}) = 4.3 \times 10^7 \text{ l d}^{-1}$$

$$\text{Industrial use: } (4.3 \times 10^7 \text{ l d}^{-1}) (1.5) = \frac{6.5 \times 10^7 \text{ l d}^{-1}}{1.1 \times 10^8 \text{ l d}^{-1}}$$

$$k_{15} = [(1.1 \times 10^8 \text{ l d}^{-1}) (1/77)] 1.8 \times 10^{11} \text{ l}$$

$$k_{15} = 7.9 \times 10^{-6} \text{ d}^{-1}.$$

4.16. k_{16} GROUND WATER TO SURFACE WATER

The movement of ground water to surface water occurs when rainwater, falling onto the $7.3 \times 10^7 \text{ m}^2$ flood plain (USDI, 1972), permeates into the ground water compartment and then overflows into the surface water compartment. A transfer also occurs through the industrial use of ground water which flows into surface water after its use. The transfer constant is based on 0.3 m of permeating rainfall/year (U.S. Army Corps Engineers, 1981) and $6.5 \times 10^7 \text{ l d}^{-1}$ of industrial pumpage (k_{15}).

Rainwater:

$$(7.3 \times 10^7 \text{ m}^2) (0.3 \text{ m yr}^{-1}) (1000 \text{ l m}^{-3}) (0.00274 \text{ yr d}^{-1}) = 6.0 \times 10^7 \text{ l d}^{-1}$$

Industrial use:

$$= \frac{6.5 \times 10^7 \text{ l d}^{-1}}{1.3 \times 10^8 \text{ l d}^{-1}}$$

$$k_{16} = 1.3 \times 10^8 \text{ l d}^{-1} / 2.7 \times 10^{11} \text{ l}$$

$$k_{16} = 4.8 \times 10^{-4} \text{ d}^{-1}.$$

4.17. k_{17} SURFACE WATER TO FISH

The calculation of the rate constant for this transfer is based on a bioaccumulation study done by Martin (1980). In closed tanks containing sheepshead minnows and channel catfish, the BaP concentration was set to 0.08 ng ml^{-1} . After 24 hr the concentration of BaP was measured in selected fish tissues, obtaining a range of concentrations for each tissue. For channel catfish the average midpoint concentration for gills, liver, gastrointestinal tract and muscle was 0.80 ng g^{-1} . For sheepshead minnows this value was 0.28 ng g^{-1} . Using these values the transfer constant was calculated as follows:

$$k_{17} = \frac{([(0.80 \text{ ng g}^{-1} + 0.28 \text{ ng g}^{-1})/2] \times (3.5 \times 10^8 \text{ g}))/1 \text{ d}}{(0.08 \text{ ng ml}^{-1}) (1.8 \times 10^{14} \text{ ml})}$$

$$k_{17} = 1.3 \times 10^{-5} \text{ d}^{-1}.$$

4.18. k_{18} SEDIMENT TO SURFACE WATER

This transfer occurs primarily through resuspension of sediment into the surface water compartment. The amount of resuspension is dependent on many parameters such as turbulence, river flow and river topography, and most of these characteristics are poorly defined for the study area. In order to estimate this transfer rate, an equilibrium constant relating the concentration of BaP in the sediment compartment to that in the surface water compartment was used. This constant is also equal to the ratio of $k_{19}:k_{18}$. Since k_{19} is known, k_{18} can be calculated. For this study the equilibrium constant was estimated on the basis of comparing observed BaP levels in sediment and river water in the Moscow River (Ilnitsky *et al.*, 1979). The transfer constant was estimated using the following relationship:

$$K = \frac{k_{19}}{k_{18}} = \frac{\text{sediment concentration}}{\text{surface water concentration}}$$

$$k_{18} = [(0.46 \text{ d}^{-1}) (0.4 \text{ ppt})] / (8400 \text{ ppt})$$

$$k_{18} = 2.2 \times 10^{-5} \text{ d}^{-1}.$$

4.19. k_{19} SURFACE WATER TO SEDIMENT

This transfer occurs as particles containing adsorbed BaP settle to the sediment at the bottom of the river. In a plot of fall velocities of quartz spheres in air and water given by Rouse (1937), a relationship exists between deposition and sedimentation velocities in which the fall velocity in air is approximately 100 times the fall velocity in water. Since the air deposition velocity was estimated to be 0.4 cm s^{-1} the sedimentation velocity can be predicted to be 0.004 cm s^{-1} . With an average river depth of 7.5 m, the transfer constant was calculated as follows:

$$k_{19} = \frac{(0.004 \text{ cm s}^{-1}) (0.01 \text{ m cm}^{-1}) (86400 \text{ s d}^{-1})}{7.5 \text{ m}}$$

$$k_{19} = 0.46 \text{ d}^{-1}.$$

4.20. k_{20} SEDIMENT OUT

BaP is transferred out of the sediment compartment in two ways; carried as suspended sediment flowing with the river out of the study area and microbial degradation.

The average suspended solids level for Huntington and Kenova (U.S. Army Corps Engineers, 1981) is 68 mg l^{-1} , and the flow rate of the Ohio river is approximately $1.8 \times 10^{11} \text{ l d}^{-1}$ (ORSANCO, 1978). Incoming suspended solids are assumed to have a BaP concentration of 80% of those leaving the area.

Herbes *et al.* (1979), determined a first order half-life due to microbial degradation of approximately $2 \times 10^4 \text{ hr}$ for BaP in sediment.

The transfer constant was calculated as follows:

$$\begin{aligned} \text{Rate of sediment removal} &= (66 \text{ mg l}^{-1}) (10^{-6} \text{ kg mg}^{-1}) (1.8 \times 10^{11} \text{ l d}^{-1}) \\ &= 1.2 \times 10^7 \text{ kg d}^{-1} \end{aligned}$$

$$\begin{aligned} k_{\text{sediment mass transfer}} &= [(1.2 \times 10^7 \text{ kg d}^{-1}) - (0.08) (1.2 \times 10^7 \text{ kg} \\ &\quad \text{d}^{-1})] / 5.0 \times 10^8 \text{ kg} \\ &= 4.8 \times 10^{-3} \text{ d}^{-1} \end{aligned}$$

$$\begin{aligned} k_{\text{microbial degradation}} &= 0.693 / (2 \times 10^4 \text{ hr} / 24 \text{ hr d}^{-1}) \\ &= 8.3 \times 10^{-4} \text{ d}^{-1} \end{aligned}$$

$$k_{20} = k_{\text{sediment mass transport}} + k_{\text{microbial degradation}}$$

$$k_{20} = 4.8 \times 10^{-3} \text{ d}^{-1} + 8.3 \times 10^{-4} \text{ d}^{-1}$$

$$k_{20} = 5.6 \times 10^{-3} \text{ d}^{-1}.$$

4.21. k_{21} FISH TO SEDIMENT

The fish to sediment transfers occur through excretion of unmetabolized BaP and by the decomposition of dead fish. Corner *et al.* (1976), reported the excretion of C-14 BaP by codfish. Almost no excretion takes place until 48 hr after ingestion, but by 96 hr after ingestion, 55% of the initial labeled compound was excreted. Based on this data a combined rate of metabolism and excretion was obtained:

$$k_{\text{combined}} = k_{\text{excretion}} + k_{\text{metabolism}} = 0.17 \text{ d}^{-1}.$$

In Corner's study, an estimated 85% of the excreted label was metabolized. Therefore,

$$k_{\text{excretion}} = 0.15 k_{\text{combined}} = 0.026 \text{ d}^{-1}.$$

The transfer rate of BaP due to decaying fish is based on an expected lifetime of 4 yr.

$$k_{\text{dying}} = [3.5 \times 10^5 \text{ kg}/(4 \text{ yr}) (365 \text{ d yr}^{-1})]/3.5 \times 10^5 \text{ kg} = 6.8 \times 10^{-4} \text{ d}^{-1}.$$

The overall transfer constant is the sum of these two values:

$$k_{21} = k_{\text{excretion}} + k_{\text{dying}} = 0.026 \text{ d}^{-1} + 0.0007 \text{ d}^{-1}$$

$$k_{21} = 0.027 \text{ d}^{-1}.$$

4.22. k_{22} FISH OUT

This transfer occurs through the metabolism of BaP within the fish. The transfer constant was based on the study by Corner *et al.* (1976) as described above for k_{21} . The estimated 85% metabolism of BaP was used to calculate this transfer constant.

$$k_{22} = k_{\text{metabolism}} = 0.85 k_{\text{combined}} = 0.85 (0.17 \text{ d}^{-1})$$

$$k_{22} = 0.14 \text{ d}^{-1}.$$

4.23. k_{23} VEGETATION OUT

This transfer occurs as BaP is metabolized by the vegetation. In a study of soybean and parsley cell suspension cultures by Trenck and Sandermann (1978), an average of 87.9% of the initial BaP remained unmetabolized after an incubation period of 38 hs. Since most of the BaP in the vegetation compartment exists as solid particulates located on leaf surfaces and in stomatal leaf openings, the metabolism rate should be much slower. Assuming a decrease in the metabolism rate of one order of magnitude, the rate constant was estimated as follows:

$$t_{1/2} = \frac{\ln [50] - \ln [100]}{(\ln [87.9] - \ln [100])/38 \text{ hr}} = 204 \text{ hr} = 8.5 \text{ d}$$

$$k_{23} = (0.693/8.5 \text{ d}) (0.1)$$

$$k_{23} = 8.2 \times 10^{-3} \text{ d}^{-1}.$$

4.24. k_{24} EDIBLE VEGETATION OUT

The same metabolism rate is assumed for edible vegetation as in k_{23} . The transfer rates are thus the same.

$$k_{24} = 8.2 \times 10^{-3} \text{ d}^{-1}.$$

4.25. k_{25} EDIBLE VEGETATION TO MAN

This transfer takes place as the vegetation grown in local gardens is consumed by the people in the area. The transfer constant is based on an annual consumption estimate of 20.4 kg of home garden grown vegetation per person (National Economics Division, 1981, and U.S. Department of Commerce, 1980). Assuming 100% of the compartment by definition is ingested per year, the transfer constant was calculated as follows:

$$k_{25} = (3.0 \times 10^6 \text{ kg}/365 \text{ d})/3.0 \times 10^6 \text{ kg}$$

$$k_{25} = 2.7 \times 10^{-3} \text{ d}^{-1}.$$

4.26. k_{26} GROUND WATER OUT

This transfer will occur due to the elimination of BaP from ground water pumped into water treatment plants for public use. The total daily water use supplied by ground water in the study area is approximately 291 l/person/day (Mason, 1978).

$$k_{26} = \frac{(291 \text{ l person}^{-1} \text{ d}^{-1}) (148\,000 \text{ persons})}{2.7 \times 10^{11} \text{ l}}$$

$$k_{26} = 1.6 \times 10^{-4} \text{ d}^{-1}.$$

4.27. k_{27} GROUND WATER TO VEGETATION

This transfer occurs during the uptake of water by vegetation. Assuming each kg of vegetation requires 0.1 kg of water per day, the transfer rate was calculated as follows:

$$k_{27} = [(0.1 \text{ kg/kg d}^{-1}) (1.0 \text{ l/kg}) (1.2 \times 10^8 \text{ kg})]/2.7 \times 10^{11} \text{ l}$$

$$k_{27} = 4.4 \times 10^{-5} \text{ d}^{-1}.$$

4.28. k_{28} SOIL TO GROUND WATER

This transfer occurs as BaP percolates through the soil column into ground water. In a report dealing with the environmental load and cycle of polycyclic aromatic hydrocarbons (PAH's), Suess (1976) suggests a transfer of PAH's due to leaching through soil layers into ground water. In the calculation of a rate constant it is assumed that percolation of BaP into ground water occurs only through the soil layers located directly above the ground water aquifer. The surface area involved is approximately 73 km², representing 4.7×10^9 kg of soil. Assuming that 0.01 of (%) of the BaP present in the soil compartment is carried into the ground water compartment by rainwater each year, the transfer constant was calculated as follows:

$$k_{28} = \frac{(4.7 \times 10^9 \text{ kg}) (0.0001 \text{ yr}^{-1}) (0.00274 \text{ yr d}^{-1})}{2.9 \times 10^{10} \text{ kg}}$$

$$k_{28} = 4.4 \times 10^{-8} \text{ d}^{-1}.$$

4.29. k_{29} MAN OUT

This transfer occurs through the metabolism of BaP and the excretion of unmetabolized BaP. The transfer rate is calculated on the basis of the disappearance rate of BaP from the body. In a study by Heidelberger and Weiss (1951), the disappearance half-life for BaP in the rat was approximately 1.75 weeks. The aryl hydrocarbon hydroxylase activities (AHH's) for man and animals have been shown to be similar in a study done by Pelkonen (1976). For this study it is assumed that the disappearance half-life for BaP in man is the same as that in the rat and other animals.

$$k_{29} = 0.693 / (1.75 \text{ wk}) (7 \text{ d wk}^{-1})$$

$$k_{29} = 0.057 \text{ d}^{-1}.$$

4.30. k_{30} GROUND WATER TO ANIMALS

This transfer takes place when animals consume water pumped from the ground water compartment. The transfer rate was calculated assuming that all water consumed by domestic livestock in the study area is supplied from ground water, and that cattle require 39 l d^{-1} and chickens require 200 ml d^{-1} (Leitch and Thomson, 1944). The average daily consumption of ground water by animals was calculated as follows:

$$2600 \text{ cattle} \times 39 \text{ l d}^{-1} = 101\,400 \text{ l d}^{-1}$$

$$900\,000 \text{ chickens} \times 0.20 \text{ l d}^{-1} = \frac{180\,000 \text{ l d}^{-1}}{281\,400 \text{ l d}^{-1}}$$

The transfer rate was then calculated as follows:

$$k_{30} = 281\,400 \text{ l d}^{-1} / 2.7 \times 10^{11} \text{ l}$$

$$k_{30} = 1.0 \times 10^{-6} \text{ d}^{-1}.$$

4.31. k_{31} AIR TO ANIMALS

This transfer occurs through inhalation and lung retention of BaP. Dukes (1953) reported that the average chicken inhales 554 ml min^{-1} . Altman and Dittmer (1972) report the average cow inhales approximately 107 l min^{-1} . Assuming 75% absorption across the lung the transfer rate was calculated as follows:

$$(900\,000 \text{ chickens}) (0.554 \text{ l min}^{-1} \text{ chicken}^{-1}) (1440 \text{ min d}^{-1}) (1.0 \times 10^{-3} \text{ m}^3 \text{ l}^{-1}) \\ = 7.2 \times 10^5 \text{ m}^3 \text{ d}^{-1}$$

$$(2600 \text{ cattle}) (107 \text{ l min}^{-1} \text{ head}^{-1}) (1440 \text{ min d}^{-1}) (1.0 \times 10^{-3} \text{ m}^3 \text{ l}^{-1})$$

$$\frac{= 4.0 \times 10^5 \text{ m}^3 \text{ d}^{-1}}{11.2 \times 10^5 \text{ m}^3 \text{ d}^{-1}}$$

$$k_{31} = [(11.2 \times 10^5 \text{ m}^3 \text{ d}^{-1}) (0.75)] / 4.9 \times 10^{11} \text{ m}^3$$

$$k_{31} = 1.7 \times 10^{-6} \text{ d}^{-1}.$$

4.32. k_{32} SOIL TO ANIMALS

This transfer occurs when animals consume soil during grazing. Miller *et al.* (1978) and Mayland *et al.* (1975) estimated soil consumption by cattle to be 0.1 to 1.5 kg per cow per day. An average value of 0.8 kg was used for this study. Assuming that grazing takes place approximately eight months per year, the average soil consumption per day was estimated as follows:

$$(0.8 \text{ kg cow}^{-1} \text{ d}^{-1}) (8 \text{ months}/12 \text{ months}) = 0.53 \text{ kg cow}^{-1} \text{ d}^{-1}.$$

The transfer constant was calculated as follows:

$$k_{32} = [(0.53 \text{ kg cow}^{-1} \text{ d}^{-1}) (2600 \text{ cows})] / 2.9 \times 10^{10} \text{ kg}$$

$$k_{32} = 4.8 \times 10^{-8} \text{ d}^{-1}.$$

4.33. k_{33} ANIMALS TO SOIL

This transfer takes place as livestock excrete unmetabolized BAP which goes into the soil. The transfer rate is based on the disappearance rate of BaP in the rat (Heidelberger and Weiss, 1951) as described in the man out (k_{29}) transfer. For a disappearance half-life of 1.75 weeks a transfer rate of combined excretion and metabolism was obtained as follows:

$$k_{\text{combined}} = k_{\text{metab}} + k_{\text{excret.}} = 0.693 / (1.75 \text{ wk}) (7 \text{ d wk}^{-1}) = 0.057 \text{ d}^{-1}.$$

Hecht *et al.* (1979), found an average of 8.8% unmetabolized (steady state) BaP in rat feces. Using this value the rate constant was calculated as follows:

$$k_{33} = (0.057 \text{ d}^{-1}) (0.088)$$

$$k_{33} = 5.0 \times 10^{-3} \text{ d}^{-1}.$$

4.34. k_{34} VEGETATION TO ANIMALS

This transfer occurs as livestock consume vegetation grown in the study area. The transfer rate was calculated assuming that 75% of the vegetation consumed by cattle and 5% of the vegetation consumed by chickens is grown within the study area. Based on data found in the Biology Data Book (Altman and Dittmer, 1972), estimated consumption of vegetation by cattle is approximately 6.5 kg d^{-1} and that by chickens is approximately 0.12 kg d^{-1} . The transfer rate was calculated as follows:

$$(0.75) (6.5 \text{ kg cow}^{-1} \text{ d}^{-1}) (2600 \text{ cow}) = 12675 \text{ kg d}^{-1}$$

$$(0.05) (0.12 \text{ kg chicken}^{-1} \text{ d}^{-1}) (900\,000 \text{ chickens}) = \frac{5400 \text{ kg d}^{-1}}{18075 \text{ kg d}^{-1}}.$$

$$k_{34} = 18075 \text{ kg d}^{-1} / 1.2 \times 10^8 \text{ kg}$$

$$k_{34} = 1.5 \times 10^{-4} \text{ d}^{-1}.$$

4.35. k_{35} SURFACE WATER TO ANIMALS

Assuming that essentially negligible amounts of surface water are consumed by animals, the transfer constant was set equal to zero.

$$k_{35} = 0.$$

4.36. k_{36} ANIMALS OUT

This transfer takes place as BaP is metabolized within animals. This calculation is again based on the disappearance half-life of BaP in the rat (Heidelberger and Weiss, 1951). The calculation is similar to that used in the man out (k_{29}) and the animal to soil (k_{33}) transfers. The value of 0.057 d^{-1} for k_{combined} was used again as follows:

$$k_{\text{combined}} = k_{\text{metab.}} + k_{\text{excreted}}$$

$$k_{36} = k_{\text{metab.}} = k_{\text{combined}} - k_{\text{excreted}}$$

$$k_{36} = 0.057 \text{ d}^{-1} - 0.005 \text{ d}^{-1}$$

$$k_{36} = 0.052 \text{ d}^{-1}.$$

4.37. k_{37} ANIMALS TO MAN

This transfer occurs through consumption of meat (beef) or eggs from within the study area. The transfer rate is calculated under the following assumptions:

(1) All milk from within the study area is shipped out for processing, milk consumed in the study area comes from outside the area (Johnson's All-star Dairy, 1981).

(2) Poultry raised within the study area are not consumed within it (County Extension Services, 1981).

(3) All eggs consumed in the area come from within the study area (County Extension Services, 1981).

(4) Five percent of the beef consumed in the area comes from within the study area.

(5) Average egg consumption is $16 \text{ kg person}^{-1} \text{ yr}^{-1}$ (National Economics Division, 1981).

(6) Average beef consumption is $54 \text{ kg person}^{-1} \text{ yr}^{-1}$ (National Economics Division, 1981).

The rate constant was calculated as follows:

$$(16 \text{ kg person}^{-1} \text{ yr}^{-1}) (148\,000 \text{ persons}) / 365 \text{ d yr}^{-1} = 6.4 \times 10^3 \text{ kg d}^{-1}$$

$$(0.05) (54 \text{ kg person}^{-1} \text{ yr}^{-1}) (148\,000 \text{ persons}) / 365 \text{ d yr}^{-1} =$$

$$\frac{1.1 \times 10^3 \text{ kg d}^{-1}}{7.5 \times 10^3 \text{ kg d}^{-1}}$$

$$k_{37} = 7.5 \times 10^3 \text{ kg d}^{-1} / 3.2 \times 10^6 \text{ kg}$$

$$k_{37} = 2.3 \times 10^{-3} \text{ d}^{-1}.$$

4.38. k_{38} GROUND WATER TO MAN

This transfer occurs through consumption of water from home wells. Assuming an estimated 20% of the population use home wells and drink 1 l of water per day the transfer constant was calculated as follows:

$$k_{38} = [(0.20) (148\,000 \text{ persons}) (1.0 \text{ l person}^{-1} \text{ d}^{-1})] / 2.7 \times 10^{11} \text{ l}$$

$$k_{38} = 1.1 \times 10^{-7} \text{ d}^{-1}.$$

4.39. k_{39} SEDIMENT TO FISH

This transfer takes place when sediment is ingested by bottom-feeding fish and passes through their gastrointestinal tract. The transfer constant is based on the following assumptions:

- (1) Seventy-five percent of the fish in the area are bottom feeders.
- (2) 0.05 kg of sediment are taken in daily per kg of fish.
- (3) Ninety-five percent of the sediment taken in is filtered out and 5% goes through the gastrointestinal tract.

The transfer was calculated as follows:

$$k_{39} = \frac{(0.05) (0.75) (0.05 \text{ kg (sediment) kg}^{-1} \text{ (fish) d}^{-1}) (3.5 \times 10^5 \text{ kg (fish)})}{5.0 \times 10^8 \text{ kg (sediment)}}$$

$$k_{39} = 1.3 \times 10^{-6} \text{ d}^{-1}.$$

A summary of transfer constants is presented in Table II.

5. Source Strengths (q values)

5.1. q_1 SOURCE TO AIR

Based on output from an Air Quality Display Model (AQDM) program (Ward and Nagda, 1979), it is estimated that 60% of the emitted BaP is removed from the study area. The AQDM uses a Gaussian diffusion equation which considers the effect of wind direction, wind speed, and meteorological stability class (National Air Pollution Control Administration, 1969). The ground level concentration values given as output from the model are independent of particle deposition velocity or size distribution. The output used in this study gave the predicted 1975 ground level BaP concentrations for the study area. Isopleths were shown for regions which had concentrations greater than 2, 5, 10, and 20 ng m⁻³. A total dimensional area which

TABLE II
BaP transfer rate constants

Rate constant	Compartment transfer	Value (d ⁻¹)
k_1	Air to Man	3.8×10^{-6}
k_2	Air to Soil	3.2×10^{-2}
k_3	Soil to Air	1.0×10^{-5}
k_4	Air to Vegetation	1.3×10^{-2}
k_5	Air to Edible Vegetation	3.2×10^{-4}
k_6	Air to Surface Water	5.3×10^{-2}
k_7	Air Out	0.00
k_8	Soil Out	1.0×10^{-3}
k_9	Soil to Surface Water	4.2×10^{-5}
k_{10}	Soil to Edible Vegetation	3.1×10^{-8}
k_{11}	Edible Vegetation to Soil	0.00
k_{12}	Soil to Vegetation	1.2×10^{-6}
k_{13}	Vegetation to Soil	2.3×10^{-3}
k_{14}	Surface Water Out	2.0×10^{-1}
k_{15}	Surface Water to Ground Water	7.9×10^{-6}
k_{16}	Ground Water to Surface Water	4.8×10^{-4}
k_{17}	Surface Water to Fish	1.3×10^{-3}
k_{18}	Sediment to Surface Water	2.2×10^{-5}
k_{19}	Surface Water to Sediment	4.6×10^{-1}
k_{20}	Sediment Out	5.6×10^{-3}
k_{21}	Fish to Sediment	2.7×10^{-2}
k_{22}	Fish Out	1.4×10^{-1}
k_{23}	Vegetation Out	8.2×10^{-3}
k_{24}	Edible Vegetation Out	8.2×10^{-3}
k_{25}	Edible Vegetation to Man	2.7×10^{-3}
k_{26}	Ground Water Out	1.6×10^{-4}
k_{27}	Ground Water to Vegetation	4.4×10^{-5}
k_{28}	Soil to Ground Water	4.4×10^{-8}
k_{29}	Man Out	5.7×10^{-2}
k_{30}	Ground Water to Animals	1.0×10^{-6}
k_{31}	Air to Animals	1.7×10^{-6}
k_{32}	Soil to Animals	4.8×10^{-8}
k_{33}	Animals to Soil	5.0×10^{-3}
k_{34}	Vegetation to Animals	1.5×10^{-4}
k_{35}	Surface Water to Animals	0.00
k_{36}	Animals Out	5.2×10^{-2}
k_{37}	Animals to Man	2.3×10^{-3}
k_{38}	Ground Water to Man	1.1×10^{-7}
k_{39}	Sediment to Fish	1.3×10^{-6}

receives BaP from within the study area was defined. A weighted average of the BaP concentrations inside the study area was divided by the sum of the weighted averages of the BaP concentrations inside and outside the study area. This provided an estimate of the percentage remaining within the area, which in this case was 40%. The input rate to air from source is based on 40% of an estimated 10 kg of total BaP emissions per day. The estimate is a sum of point source emission data (Ward and Nagda, 1979) plus an estimate of area source emissions shown on previous maps

displaying these sources with relative intensities. Point source emissions are estimated to be approximately 6 kg per day and area source emissions are estimated to be 4 kg d⁻¹ for a total of 10 kg d⁻¹. Work reported by Korfmacher *et al.* (1980) indicated that a 16% total reduction of BaP adsorbed on fly ash will occur during the time it takes to deposit. Accordingly the input source strength was reduced by 16%. From these estimates a source strength of 3.4 kg d⁻¹ was obtained.

5.2. q_2 SOURCE TO SURFACE WATER

Input to surface water occurs through industrial effluents containing BaP. Both Harrison *et al.* (1975) and Andelmann and Suess 1970 studied polycyclic aromatic hydrocarbon contamination of industrial wastewaters. A table summarizing their results showed BaP concentrations of 12 to 16 µg l⁻¹ and an industrial pumpage rate of 6.5×10^7 l per day. The estimated source strength from source to surface water is 0.9 kg d⁻¹.

6. Results and Discussion

Given the source input strengths, transfer rate constants, and compartment masses of volumes, steady state concentration values can be obtained for BaP. An equation relating the rate of change of BaP mass in a compartment with respect to time as a function of these parameters was expressed for each compartment (Table III). By applying the steady state approximation to this set of equations the rates of change

TABLE III
Steady state equations

$$\begin{aligned} dQa/dt &= q_1 + k_3Qb - Qa(k_1 + k_2 + k_4 + k_5 + k_6 + k_7 + k_{31}) = 0 \\ dQb/dt &= k_2 + Qa + k_{13}Qe + k_{11}Qf + k_{33}Qh - Qb(k_3 + k_9 + k_{10} + k_{12} + k_8 + k_{28} + k_{32}) = 0 \\ dQc/dt &= q_2 + k_6Qa + k_9Qb + k_{18}Qd + k_{16}Qi = Qc(k_{14} + k_{19} + k_{17} + k_{15} + k_{35}) = 0 \\ dQd/dt &= k_{19}Qc + k_{21}Qg - Qd(k_{18} + k_{20} + k_{39}) = 0 \\ dQe/dt &= k_4Qa + k_{12}Qb + k_{27}Qi - Qe(k_{13} + k_{34}) = 0 \\ dQf/dt &= k_5Qa + k_{10}Qb - Qf(k_{11} + k_{24} + k_{25}) = 0 \\ dQg/dt &= k_{17}Qc + k_{39}Qd - Qg(k_{21} + k_{22}) = 0 \\ dQh/dt &= k_{31}Qa + k_{32}Qb + k_{34}Qe + k_{35}Qc + k_{30}Qi - Qh(k_{33} + k_{36} + k_{37}) = 0 \\ dQi/dt &= k_{28}Qb + k_{15}Qc - Qi(k_{16} + k_{26} + k_{27} + k_{30} + k_{38}) = 0 \\ dQj/dt &= k_1Qa + k_{25}Qf + k_{37}Qh + k_{38}Qi - k_{29}Qj = 0 \end{aligned}$$

Definitions

- Q_2 = Mass of BaP in compartment 2 in kg
 q_1 = Source input strength to the air compartment in kg d⁻¹
 q_2 = Source input strength to the surface water compartment in kg d⁻¹
 k_i = Transfer rate constant number i in d⁻¹

Compartments

A	Air	F	Edible vegetation
B	Soil	G	Fish
C	Surface water	H	Animals
D	Sediment	I	Ground water
E	Vegetation	J	Man

were set equal to zero. The equations were then solved simultaneously to yield the mass quantity of BaP in each compartment. The mass quantity was divided by the compartment mass or volume to yield the steady state BaP concentration. Table IV presents the calculated steady state concentration values.

6.1. SENSITIVITY ANALYSIS

After the state concentration values were obtained, a sensitivity analysis was performed to determine which rate constants most affected each of the concentration values. In this analysis each transfer rate constant was individually increased by 10% prior to calculation of the steady state concentrations. The percent change in concentration was then calculated for BaP levels that were significantly changed by the increase of rate constant. A significant change was defined as an increase or decrease in the last significant digit of the concentration value. A summary of this analysis is presented in Table V.

A BaP concentration value of 19 ng cm^{-3} was calculated for the air compartment. The increase in the air to soil (k_2) rate constant has the greatest effect on this concentration; a 6% decrease was noted. The change in the air to surface water (k_6) and the air out (k_7) rate constants both led to 5% decreases in concentration.

The soil compartment had a calculated BaP concentration of $92 \text{ } \mu\text{g kg}^{-1}$. The increase in the soil out (k_8) rate constant caused a 10% decrease in concentration. The BaP concentration in the surface water compartment was calculated to be 12 ng L^{-1} . The increase of the k_2 , k_8 , k_{14} , and k_{19} rate constants each yielded an 8% decrease in this concentration.

TABLE IV
BaP steady state concentration values

Air	19	ng m^{-3}
Soil	92	$\mu\text{g kg}^{-1}$
Surface water	12	ng l^{-1}
Sediment	2500	$\mu\text{g kg}^{-1}$
Vegetation	99	$\mu\text{g kg}^{-1}$
Edible vegetation	95	$\mu\text{g kg}^{-1}$
Fish	28	$\mu\text{g kg}^{-1}$
Animals	10	$\mu\text{g kg}^{-1}$
Ground water	0.74	ng l^{-1}
Man	1.6	$\mu\text{g kg}^{-1}$

The sediment compartment has a calculated BaP level of $2500 \text{ } \mu\text{g kg}^{-1}$. The sediment out (k_{20}) rate constant has the greatest effect on this level; an 8% decrease was noted. The increase in the air to surface water (k_6), soil to surface water (k_9), and surface water to sediment (k_{19}) rate constants all yielded 3% changes in concentration.

The level of BaP in the vegetation compartment was calculated to be $99 \text{ } \mu\text{g kg}^{-1}$. Changes in air to soil (k_2) constant and vegetation out (k_{23}) led to an 8% decrease, while the change in the air to vegetation (k_4) constant led to a 9% increase in BaP

concentration. The edible vegetation compartment had a calculated BaP concentration of $95 \mu\text{g kg}^{-1}$. The change in air to edible vegetation (k_5) caused a 10% increase while the change in edible vegetation out (k_{24}) caused a 7% decrease in BaP concentration. The change in the air to soil (k_2) rate constant yielded a 7% decrease in the BaP level.

TABLE V
Sensitivity analysis

Compartment	Rate constant (k) altered	Resulting conc. change (%) in compartment
Air	2	- 6
Soil	2	+ 1
	6	- 2
	8	- 10
	9	- 1
Surface Water	2	+ 8
	8	- 8
	14	- 8
	19	- 8
Sediment	2	+ 3
	6	+ 3
	14	- 3
	19	+ 3
	20	- 8
Vegetation	2	- 8
	4	9
	6	- 1
	13	- 2
	23	- 8
Edible Vegetation	2	- 7
	5	+ 10
	6	- 1
	10	+ 1
	24	- 7
	25	- 2
Fish	2	- 2
	6	+ 2
	14	- 2
	17	+ 2
	19	+ 2
	20	- 9
	21	- 2
	22	- 9
	39	+ 9
Animals	2	- 7
	4	+ 8
	6	- 2
	8	- 1

Table V (continued)

	13	- 2
	23	- 7
	33	- 1
	34	+ 8
	36	- 8
	37	- 1
Ground Water	2	+ 1
	8	- 7
	15	+ 1
	16	- 5
	26	- 1
	28	+ 9
Man	2	-13
	5	+ 7
	6	- 7
	8	- 7
	23	- 7
	24	- 7
	29	-13
	36	- 7

For the fish compartment, a BaP level of $28 \mu\text{g kg}^{-1}$ was calculated. The changes in the sediment to fish (k_{39}), sediment out (k_{20}), and the fish out (k_{22}) all gave 9% changes in BaP concentration.

A BaP concentration of $10 \mu\text{g kg}^{-1}$ was calculated for the animals compartment. Changes in the constants for both air to vegetation (k_4) and for vegetation to animals (k_{34}) increased the level of BaP by 8%. An 8% decrease in BaP concentration was noted due to the change in animals out (k_{36}). The increase in both the vegetation out (k_{23}) and the air to soil (k_2) constants led to 7% decreases in BaP level. The changes in air to surface water (k_6), soil out (k_8), and vegetation to soil (k_{13}) constants each caused minimal changes in the BaP concentration.

The calculated ground water BaP level was 0.74 ng l^{-1} . A 7% decrease in concentration was noted for the change in the soil out (k_8) constant and the change in the soil to ground water (k_{28}) constant caused a 9% increase. The increase in the ground water to surface water (k_{16}) constant resulted in a 5% decrease in BaP concentration.

The man compartment had a calculated BaP concentration of $1.6 \mu\text{g kg}^{-1}$. The BaP level is significantly affected by 8 transfer rate constants. The constants which most influences this level are for man out (k_{29}) and the air to soil (k_2). It should be noted that all of the changes in this compartment are decreases except in the case of k_5 , air to edible vegetation.

The change in the air to surface water (k_6) transfer rate constant significantly affected the BaP level in 7 of the compartments, the air to soil (k_2) constant all 10 compartments, and soil out (k_8) affected 5. The rate constants for soil to air (k_3), edible vegetation to soil (k_{11}), surface water out (k_{14}), surface water to fish (k_{17}), sediment to surface water (k_{18}), fish to sediment, ground water to animals (k_{30}), air

to animals (k_{31}), animals to soil (k_{33}), and ground water to man (k_{38}) when altered by 10% had little significant effect on the BaP level in any of the compartments except in isolated cases.

6.2. COMPARISON WITH MEASURED CONCENTRATIONS

This analysis was conducted without access to field collected data from the study area. Although such data is normally included for these analyses, one of the purposes in this case was to examine the efficiency of the approach when there is no site specific monitoring data.

Table VI presents average values of data from samples collected in the study area. The sampling parameters must be described, because the data cannot be considered spatially and temporally representative of the area in all aspects. For example, the air data are from HI-Volume samples, approximately 1/2 of which were taken every two weeks for a six month period of October through March. The remainder resulted from an intensive two week sampling during the month of April. During the routine sampling, three Hi-Volume samplers were in operation, two in the river valley (one at each end of the study area) and the other on the edge of the area.

The data for soils, vegetation, surface water, and sediment are the most spatially representative. The latter two media were sampled exactly as fitting the earlier descriptions of their compartment sizes. Soil and vegetation were not sampled in the eastern 1/4 of the study area.

Surface water and sediment were collected during two sampling events, but both occurred at approximately the same time of year, March 1981 and April 1980. Soil and vegetation were also sampled twice, once in the fall (Oct./Nov.) and again in the spring (Apr./May).

TABLE VI
Averages of measured BaP concentrations in several media of the seosa^a

Medium	Observed value	Number of samples	Maximum value
air	5 ng m ⁻³	67	39 ng m ⁻³
soil	1333 µg kg ⁻¹	75	45794 µg kg ⁻¹
soil ^b	446 µg kg ⁻¹	73	4569 µg kg ⁻¹
surface water	33 ng l ⁻¹	61	140 ng l ⁻¹
sediment	463 µg kg ⁻¹	68	7893 µg kg ⁻¹
sediment ^b	351 µg kg ⁻¹	67	2570 µg kg ⁻¹
vegetation	38 µg kg ⁻¹	283	874 µg kg ⁻¹
fish ^c	<25 µg kg ⁻¹	4	<25 µg kg ⁻¹

^a See text for discussion of sampling parameters.

^b See text for discussion of outlying values.

^c Minimum detection limit for this medium.

Two extraordinary high values were obtained from soil and one from sediment. The second entries for these media in Table VI are calculated excluding the outlier

data. It is obvious that these outliers have a large impact on the average concentration of BaP in soil. The maximum values with and without the outliers differ by an order of magnitude.

A critical review of all phases of sampling and chemical analysis did not provide justification for discarding the outlier values. However, samples taken at the same locations at a different sampling period gave values smaller than an order of magnitude less than the outliers. Also, a geostatistical analysis (kriging) of the soils data clearly shows the abnormality of these two data points. For the purposes of this analysis, it should be appropriate to disregard the soil outliers.

The case of a possible outlier in sediment is less clear because the value is less extreme. The maximum values differ only by about three fold and the impact on the average is not large. In this case it should be appropriate to retain the value.

7. Conclusion

In general, the steady state concentrations in Table IV (calculated) and the observed values in Table VI compare favorably considering the approach dictated for this analysis and the paucity of data about the study area. The greatest differences observed were those of soil and sediment which varied by factors of 4.8 and 5.4 respectively. With respect to soil, deviations between the two values were expected as the majority of samples taken were in the highly industrialized and populated areas. Thus the observed value would be skewed to a higher value than that calculated for the entire area. In general, the control area soil samples were as much as 10-fold lower than the Ashland samples (Site 4, Figure 2). The difference in the two values for the sediment BaP levels may be due to a combination of variables, including the estimate of compartment size, inhomogeneity of the sampling regime, and/or the inappropriate estimation of associated rate constants. For the compartments other than soil and sediment, reasonable agreement was observed for the calculated and observed levels of BaP.

It is interesting to note from the sensitivity analysis that increased rate changes for 8 of the pathways have greater impacts on the BaP levels in man than does a like change in the direct inhalatory pathway, air to man. Seven of the pathways either remove BaP from the system or divert it from man, so in these cases, the concentration in man is decreased. However, increasing the rate from air to edible vegetation increases the BaP level in man. Critical examination of data such as these may suggest a more cost effective monitoring of media alternate to the most direct or apparently obvious.

In conclusion, comparison of the two sets of data indicates that the kinetic analysis technique can successfully be applied to the pre-sampling estimation of the distribution of organic contaminants in environmental systems. This must be qualified by any lack of literature information regarding the processes that affect the environmental fate of a selected pollutant.

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