FINAL REPORT

THE EXPOSURE OF THE NEW YORK CITY WATERSHED TO PCBs EMITTED FROM THE HUDSON RIVER

June 2000

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THE EXPOSURE OF THE NEW YORK CITY WATERSHED TO PCBs EMITTED FROM THE HUDSON RIVER

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SUMMARY

This project has evaluated the exposure of the New York City watershed to a hitherto unexamined source of toxic contamination: the deposition on the watershed of airborne polychlorinated biphenyls (PCBs) that are emitted from the Hudson River. Because of the 0.2 to 1.3 million pounds of PCBs (an EPA estimate) discarded into the river from nearby General Electric plants between 1957 and 1975, the river still exceeds the Federal water quality standard; fish consumption is restricted, and public hearings have been held to assess G.E.'s liability for the ecological damage to this major natural resource. However, the assessment has not yet considered the ecological impact on the New York City watershed of the PCBs that the river emits into the air – which in 1997 amounted to about two-thirds of the PCBs dissolved in the river.

This project is an initial effort in this direction. For this purpose, an air transport model was used to track the PCBs emitted from successive 10-mile sectors of the river to each of the reservoirs and basins that comprise the overall watershed system. The results generated by the model and by analyses of airborne PCBs sampled at a river site (Coeymans) and at a site in the Neversink watershed (Frost Valley) show that the watershed is systematically exposed to airborne PCBs emitted from the Hudson River.

The results also show that the airborne PCBs that have been deposited on the watershed, chiefly the more highly chlorinated (and generally more toxic) congeners, tend to accumulate there – for example, in vegetation, soil and reservoir sediments. In warm summer temperatures the accumulated PCBs vaporize; re-emitted into the air, they give rise to the unusually high airborne PCB concentration that we have measured at Frost Valley in the Neversink watershed: 1740 picograms per cubic meter. This reflects the long-term accumulation and revolatilization process that has been underway since the Hudson River was first heavily contaminated with PCBs in 1957.

The exposures of the different watershed reservoirs and basins to the airborne PCBs emitted from the Hudson River vary considerably. The Croton/Kensico watershed lies east of the river. It is exposed to particularly large amounts of airborne PCBs from the Hudson River because, compared to the Delaware/Catskill watershed, which is west of the river, it is relatively close to it and generally subject to eastward, more intense, winds (at least during our study period). The reservoirs in this watershed, which account for only 21% of the volume of the total system, receive 80% of the total deposition of airborne PCBs transported from the Hudson River to both watersheds. As a result, PCB concentrations in the reservoirs of the Croton/Kensico system may be several times greater than the concentration in the Delaware/Catskill reservoirs.

The sequential events that have contaminated the watershed with airborne PCBs emitted from the Hudson River are consistent with the known facts about the

physical processes that govern the environmental fate of PCB: the effect of ambient temperature on the volatility and deposition of the different PCB congeners; increased dispersion and therefore decreased deposition, with distance between the river (the source) and the watershed sites (the receptors); the impact of wind speed and direction on deposition intensity at the receptors.

In sum, these results redefine the ecological domain affected by the PCBs originally discarded into the upper Hudson River. In the river they have led to the formation of a "sink" of heavily contaminated sediment in the pool above the Thompson Island dam, which continues to release unacceptable levels of PCBs into the downstream sections. It now appears that this ecological hazard extends beyond the river itself. Just as the accumulated PCBs have caused the river to serve as a source of airborne PCBs, so too, the accumulated PCBs in the watershed, for example at Frost Valley, have been re-emitted, accounting for most of the airborne concentration at that site. Ironically, it is likely that some of this airborne PCB, carried eastward by the prevailing winds, is redeposited in the river, thereby counteracting to a degree the PCB volatilization that has helped to reduce the PCB level in the river water.

Finally, we note that the existence of this enlarged PCB-contaminated ecological domain is thus far based on an air transport model – an inherently indirect method of assessing PCB deposition and accumulation. Accordingly, this assessment should be confirmed by direct measurements of PCB accumulation in the watershed. This can be done, for example, by measuring the PCB content of reservoir sediments and tree bark (which is known to accumulate PCBs); in both cases dating techniques can be used to delineate the history of PCB accumulation (in sediments, by serial analysis of layers; in tree bark, by comparative analysis of bark from trees of different ages).

I. INTRODUCTION

This project was designed to assess the degree to which the New York City watershed – the source of the city's water supply – is exposed to airborne polychlorinated biphenyls (PCBs) originating in the Hudson River and the potential environmental impact of this exposure. This is a particularly timely issue. As provided by the Federal Superfund Program, New York State is now participating in a Natural Resource Damage assessment to determine the total effect of Hudson River PCB contamination on the state's natural resources. This is an important prelude to assessing the resulting liability on the part of the firms – General Electric in particular – that have released large amounts of PCBs into the river. However, thus far the damage assessment has considered only the effects resulting from direct contact with contaminated river water and/or sediment. Although there is no such direct contact between the watershed and the river contaminants, it has been established that the discarded industrial PCBs have become concentrated in the Hudson River sediments, that they dissolve in the river water – and are then emitted into the air. Once in the air, PCBs could readily travel the relatively short distances that separate the Hudson River from the New York City watersheds (see Figure 1) and become deposited there. This project is an initial effort to evaluate this potentially serious environmental process.

II. BACKGROUND

PCBs are similar to a group of other chlorinated environmental pollutants such as dioxin and DDT in their persistence and toxicity. But in other ways PCBs are unusual: They were first produced and used commercially in 1929, long before most other such synthetic chlorinated compounds entered the environment; although their production was banned in 1977, more than half of the one billion pounds of PCB produced until then have been released into the environment.

In recent years, a good deal has been learned about the environmental behavior of PCBs from studies of their tendency to concentrate in the Arctic, despite the very limited PCB sources that occur in that region. It is now known that PCBs are carried in the air from sources as distant as the United States to the Arctic; there, because of the low ambient temperature, they tend to deposit and accumulate in the food chains that support people and wildlife. In the Canadian Arctic, PCBs have been associated with low birth weight and immune deficiencies in Inuit infants and with developmental abnormalities in polar bears. Relatively low temperatures also occur at high altitudes, and a recent study shows that PCBs tend to preferentially deposit from the air and accumulate in the Canadian Rockies, just as they do in northern latitudes. (1)

The environmental behavior of PCBs reflects the physical and chemical properties of this family of over 200 separate molecules (congeners). These properties

fig 1

are largely governed by each congener's molecular structure, in particular the number and location of its chlorine atoms. As a result, PCB congeners vary considerably in their properties and hence in their environmental behavior. For that reason, in this study we have evaluated the air transport characteristics of the individual congeners that comprise the molecular family of PCBs.

The degree to which a PCB congener exists as a vapor and therefore tends to remain airborne, or attaches to airborne particles (e.g. dust) and therefore tends to deposit is a particularly important property. This property varies considerably with temperature; the <u>critical temperature</u> (Tc) – the temperature at which half of the congener molecules are in the form of vapor and half attached to particles – is a useful means of characterizing this effect. (2)

In the environment – for example, dissolved in the Hudson River or airborne above it – PCBs exist as a mixture of congeners. Such a mixture can be identified by its "profile" – the relative amounts of each of the congeners, ordered according to their "BZ number." This number has been assigned by international convention to each congener and generally increases with the molecule's structural complexity and the number of chlorine atoms. The critical temperature rises with the number of chlorines, so that for a typical trichlorinated PCB (BZ19) Tc is -41^{o}C; for a tetra-chlorinated congener (BZ52), -24^{o}C; for a hepta-chlorinated congener (BZ180), +13^{o}C. Thus, in the temperate climate characteristic of the New York watershed, it is chiefly the more highly chlorinated PCB congeners (BZ above 77), which, when airborne, will tend to attach to particles, deposit and accumulate. The greater the degree of chlorination and critical temperature, the greater the tendency to deposit – and the less the tendency to revolatilize from the accumulated deposit and become airborne. In the New York region, the mono-, di-, tri- and tetra-chlorinated congeners will largely exist as vapor until, by moving northward, they reach Arctic temperatures of -40^{o}C or less and are deposited.

In temperate regions PCB congener behavior will also depend on seasonal and even daily changes in temperature. For example, especially in the warm summer months the moderate to highly chlorinated PCBs in contaminated areas will volatilize to a degree and become airborne. Carried northward – or to higher altitudes – and thus to cooler regions, the PCBs are deposited; then in the next summer they can revolatilize and again move to cooler areas, generally northward. The least chlorinated PCBs revolatilize <u>throughout</u> the seasons due to their low critical temperatures (Tc is -50°C for mono-chlorinated PCBs). These PCBs therefore move rapidly to the coolest regions. This process, which is now known as the "grasshopper effect," has been underway since PCBs were first produced in 1929, contaminating not only cooler regions in the United States and the Arctic, but – as they are deposited en route – to some degree every square meter of soil and vegetation.

These phenomena, and the complex ways in which they interact, govern the movement of PCB from any given source to any given receptor. As a result, the same place may serve as a source and emit PCBs into the air when it is warm and act as a receptor onto which airborne PCBs are deposited when it is cold.

The PCB contamination of the Hudson River has been intensively studied in recent years. EPA-sponsored studies show that most of the PCBs dumped into the upper Hudson River are now attached to the sediments in the pool behind the Thompson Dam, about 10 miles south of Hudson Falls. Over time, this deposit has released dissolved PCBs into the water, which, flowing over the dam, has carried them downstream into New York Harbor. Detailed reports prepared for EPA describe the concentrations of PCBs in sediment and water at a series of sectors along the length of the river. (3) The mixture of these congeners originally dumped into the river at the General Electric plants at Hudson Falls and Fort Edwards is distinctive in its profile. At present, the PCBs found in the river sediment are characterized by a profile which resembles that of the original mixture, but with a higher proportion of mono-, di-, tri- and tetra-chlorinated congeners – the result of partial anaerobic bacterial dechlorination of the more highly chlorinated congeners in the sediments.

In this study we have used two basic methods, which are described in the Appendix, to investigate the movement of airborne PCBs from the river to the watershed. (a) An air transport model was used to estimate the amounts of PCBs deposited on the system's reservoirs and their respective watershed basins from the airborne PCBs emitted by the Hudson River. (b) Daily samples of air were collected for chemical analysis at a site on the bank of the Hudson River and at a site in the Delaware/Catskill watershed over a four-week period in August/September 1998. The concentration of each of the congeners detected in each of these samples was determined and expressed as the amount present per cubic meter of air. This yielded the congener profile and concentration of the airborne PCBs at both sites. The studies based on these two procedures and their results are described below.

III. RESULTS

A. PCB Transport from a Site on the Hudson River (at Coeymans) to a Site in the Neversink Watershed Basin (at Frost Valley):

In order to directly characterize the airborne PCBs at the Hudson River and in a typical watershed site, samples were taken daily from August 24,1998 to September 21, 1998, at a riverside site at the town of Coeymans just below Albany and from August 26 to September 22 at Frost Valley in the Neversink watershed. As described in the Appendix, at each site air was drawn through an adsorbent cartridge during each successive 24-hour period; the PCBs were later extracted and the concentrations of each of the congeners detected expressed as picograms (trillionths of a gram) per cubic meter of air (pg/m^3). As shown in Figure 2A, at the Coeymans site, the daily congener profiles exhibit a general similarity; they are characterized by appreciable concentrations of certain congeners in the range of BZ1-70 and by lower levels at the higher BZ numbers. In contrast, the Frost Valley congener profiles (see Figure 2B) exhibit relatively higher concentrations of congeners in the range beyond BZ77. These differences in the congener profiles from the two sites can be seen more clearly in Figure 3, in which the average congener concentrations of the daily profiles are compared. The average daily total PCB concentration was 1760 picograms per cubic meter at Coeymans and 1740 picograms per cubic meter at Frost Valley.

The profile at Coeymans reflects the composition of the PCBs originally dumped into the river, modified by the subsequent bacterial action that removed chlorine atoms from some of the highly chlorinated congeners, enhancing the levels of mono-, di-, tri- and tetra-chlorinated congeners. This accounts for the relatively high congener concentrations at BZ17-19 (trichlorinated) and BZ42-52 (tetra-chlorinated). Congeners above BZ77, which are present in relatively low concentrations, include the penta-, hexa- and hepta-chlorinated PCBs. In what follows, we consider the origin of the airborne PCBs at Coeymans from the river water, their transport in the air to the Frost Valley monitoring site, and their subsequent fate at that site.

1. The emission of PCBs from Hudson River water into the air:

In assessing the transport of PCBs emitted from the Hudson River to the watershed, it is necessary to determine both the profile of the emitted congeners (i.e., their relative airborne concentrations) and their overall rate of emission from the river, since these data are needed to model the amounts of airborne PCB congeners that are deposited on the various watershed sites.

According to a recent EPA report (4), airborne PCB congeners collected at the Hudson River represent the PCBs that volatilize from the river water. We assume that this generalization applies as well to the airborne PCBs that we have sampled daily in August/September 1998 at the Coeymans river site. Accordingly, the average congener profile of these samples (see Figure 3) is regarded as representative of the profile of the PCBs emitted from the river as a whole.

A model-based analysis recently reported by Farley (5) characterizes the complex pathways that govern the movement of PCBs within the Hudson River. Figure 4, which is reproduced from Farley's report, describes the movement of PCBs in 1997 in the section of the river extending from Troy to the New York City line. It shows that 65% of the total PCBs in the water column was emitted into the air through volatilization. Farley's analysis of the volatilization process leads to the generalization that the rate of emission of PCBs into the air, in grams per day, is given by the amount

fig 2a

fig 2b

fig 3

fig 4

(in grams) of PCBs dissolved in the upper 0.5 cubic meter layer of the water column. However, in his analysis of PCBs dissolved in the water, the various congeners were not considered individually but as homolog groups consisting of all the congeners with the same number of chlorine atoms per molecule. In addition, several homolog groups were omitted from the analysis. For our purpose it was necessary to relate the total PCB emission rate to a congener-by-congener profile of the emitted material. Accordingly, Farley's emission data were modified by adding the missing homologs (mono, hepta, octa and nona) and disaggregating the homolog groups into their constituent congeners, using the congener proportionality shown in the Coeymans profile as a guide. These procedures produced, for each 10-mile section of the Hudson River analyzed by Farley, an estimated rate of emission for the complete congener profile observed in the airborne PCBs measured at Coeymans.

2. The transport of airborne PCBs from the Hudson River to the Neversink basin at Frost Valley:

As indicated earlier, the HYSPLIT model can be used to trace PCBs from any source, in this case the PCBs emitted from the river at Coeymans, to any receptor site, in this case, a monitoring station at Frost Valley in the Neversink basin. The efficiency of air transport is expressed as the Air Transport Coefficient (ATC) – that is, the fraction of a unit amount of PCBs emitted at the source that reaches the receptor as either airborne or deposited congeners.

The concentration of airborne congeners is affected by diffusion and dispersion, which sharply reduces concentration with increasing source-receptor distance, by advection (wind-impelled movement), and by destructive reactions, predominately with airborne hydroxyl radicals. The efficiency of deposition is strongly affected by the congener's physical state – particularly, whether it is in the vapor phase or bound to airborne particulates – which in turn is affected by the ambient temperature.

Deposition is considerably enhanced when the congener is bound to particles. Congeners differ sharply in this respect. The temperature coefficient (Tc) of different PCB congeners – that is, the temperature at which 50% of the congener is in the vapor phase and 50% particle-bound – varies from +30^{o}C to -50^{o}C. (2) Air transport efficiency is also affected by weather conditions. Wind direction determines whether PCBs emitted from the source are directed toward or away from the receptor; rain and snowfall may considerably enhance the deposition of particle-bound congeners. Finally, deposition is considerably influenced by ground conditions at the site; soil, vegetation and surface water vary considerably in their affinity for PCB vapor and particle-bound PCB.

Two sets of model runs were carried out to estimate and compare the air transport coefficients for representative PCB congeners from the same site over two different time periods – five weeks and one year. One set of runs evaluated the ATCs for transport of eight congeners from the Coeymans site to the Frost Valley site during the period August 20 to September 25, 1998. A second set of runs evaluated the ATCs for 12 congeners, emitted from the river at the Coeymans site to Frost Valley over the one-year period, March 1998-February 1999.

The two sets of runs are governed by different conditions. In comparison with the August/September model run, the one-year run involves a wider range of weather conditions, especially with respect to rainfall and snow (the August/September 1998 test period was relatively dry) – conditions that enhance deposition. In comparison with emissions from a relatively close 10-mile sector of the river. emission from the entire river involves a longer average source-receptor distance; the ATC decreases exponentially with distance. Finally, the wider range of ambient temperature and precipitation over the one-year model run will accentuate the variable responses of the different congeners to these factors.

Despite these inherent differences in the governing conditions of the two model runs, they yielded comparable results. As shown by Figure 5A, in both cases the efficiency of air transport that culminates in congener deposition increases with the congener’s critical temperature (Tc) and hence with its BZ number. In contrast, the ATC values for airborne congener concentration (see Figure 5B) is much less affected by Tc and is characterized by a maximum at congener BZ52-70. This indicates that congeners above this critical range, i.e. BZ99-180, are preferentially deposited in sufficiently high proportions to reduce the overall concentration of the airborne congeners by the time they reach Frost Valley, thereby reducing the net efficiency of air transport.

Thus, we may visualize the transport of the PCBs emitted at the Hudson River to Frost Valley in the following way. As a unit volume of air – let us say, one cubic meter – containing the mixture of PCBs characterized by the measured airborne profile at Coeymans moves through the air to Frost Valley several major changes occur. En route, the higher group of congeners (BZ99-180) tend to bind to airborne particles and therefore to deposit, so that the airborne concentration of the overall congener profile is reduced to a degree by the time Frost Valley is reached; the lower congeners are less affected by this process. When the airborne congeners reach the Frost Valley site itself, the higher congeners are preferentially deposited and contaminate the soil and vegetation at the site. At Frost Valley the lower congeners have a greater tendency to remain airborne in the vapor state and, depending on weather conditions, a greater proportion may therefore leave the site.

These model-based observations suggest that, in comparison with the measured profile of airborne PCB concentrations at the Hudson River (at Coeymans), the corresponding profile measured at Frost Valley – to the extent that it includes figs 5a-b

congeners transported from the river – should be somewhat depleted in its higher congeners because of their tendency to deposit en route and at the site itself. However, a comparison of the profiles based on concurrent measurements of PCB concentrations at the two sites (see Fig. 3) indicates, instead, that the concentrations of the higher congeners at Frost Valley are significantly greater than their concentration at Coeymans. This distinction between the higher and lower groups of congeners is delineated in Figure 6, which describes the difference between the two measured profiles as the ratio of congener concentrations: Frost Valley/Coeymans. The ratio is variable, but generally below 1.0 in the low congener group (BZ1-70), rising to a positive value (about 3.0) between BZ52 and BZ70, which is maintained as BZ number rises. This is additional, independent, evidence of the critical significance of the BZ52-70 congeners as the demarcation between the lower and higher congener groups that was suggested by the air transport coefficient data.

Additional evidence regarding the significance of this critical distinctions between the lower and higher congener groups is presented in Figure 7. This shows that there is no systematic relationship between the relative concentrations of individual congeners in the lower BZ groups measured at Coeymans and Frost Valley; the regression coefficient, R^2, is only 0.0031. In contrast, the relative concentrations of the higher group of congeners above BZ70 are highly correlated: R^2 is 0.85, signifying that 85% of the relative congener-to-congener variation within this group in the Frost Valley sample is accounted for by the comparable variation in the Coeymans sample. This close resemblance between the congener profiles above BZ70 is consistent with the transport of these higher PCB congeners from the Hudson River to Frost Valley. But the lack of correlation between the lower groups of congeners in the profiles suggests that the overall relation between the two profiles is more complex.

In sum, while there is evidence that the airborne PCBs that originate in the Hudson River water are transported through the air to the Neversink watershed basin at Frost Valley, some other process must have enhanced the airborne concentration of the higher congeners at that site. This process is considered in what follows.

3. The fate of Hudson River PCBs in the watershed:

PCBs transported in the air from the Hudson River to a watershed site such as Frost Valley arrive in the form of vapor or bound to particles. Those less-chlorinated congeners that exist as vapor at the Frost Valley ambient temperature during the August/September test period are therefore more likely to remain airborne and – subject to weather conditions – to leave the area. The less-chlorinated congeners that do adsorb to vegetation and soil in the vapor state will soon revolatilize and be carried away from the site.

The more chlorinated (higher BZ number) congeners that arrive in the particulate

fig 6

fig 7

form or become bound to particles on reaching the relatively low temperature at Frost Valley tend to deposit and become incorporated into the soil and vegetation. The higher group of congeners that tend to deposit are chemically stable and will accumulate at the site over time, beginning in the 1950s when the river was first heavily contaminated with PCBs. In sum, we can expect that in general, over time, the higher group of congeners (generally above BZ70) has accumulated at Frost Valley.

In considering the further fate of these congeners, it is useful to examine in more detail how the ambient temperature affects their physical state. As noted earlier, the ambient temperature has important effects on the environmental behavior of PCBs. Temperature governs the tendency of airborne congeners to bind to particles and hence to become deposited; binding decreases with rising temperature. Temperature also affects the volatilization of PCBs; volatilization, as indicated by vapor pressure, increases with rising temperature.

From the available data on the physical properties of PCBs, it is possible to describe the relationship between the percent of a congener that is associated with particles and the ambient temperature. This is shown in Figure 8 for each of 10 representative congeners. It is apparent that especially in the range of temperatures characteristic of the Hudson River and the Neversink watershed basin in the August/September 1998 study period, there is a sharp distinction between the behavior of the lower (BZ1-70) and higher (BZ99 and above) groups of congeners. For example, in the range that includes the ambient temperatures at Coeymans and Frost Valley, 20°-30°C (68°-86°F), the percent of the lower congeners in the particulate phase is close to zero. In contrast, at that same temperature range the percent of the higher congeners bound to particles at 20°C ranges from 3% (BZ99) to 35% (BZ180).

There is a corresponding difference in the response of the two groups of congeners to the shift in temperature between their origin at Coeymans (averaging 29°C during the test period) and their arrival at Frost Valley (averaging 26°C at the same time). The lower congeners are almost completely in the vapor phase at both sites, while the percent of the higher congeners in the particulate phase increases from an average of 17% to 23% on reaching the relatively low temperature at Frost Valley. In sum, en route from the Hudson River to Frost Valley and at that site itself, virtually only the higher group of congeners (BZ99 and above) will be bound to particles and hence likely to be deposited to the surface at a greater rate than the lower congener group.

As noted above, it has been found that in the warm summer months, PCBs in heavily contaminated areas tend to volatilize and become airborne. (6) This suggests that the airborne PCB profile measured at Frost Valley in August/September 1998 includes a mixture of airborne PCBs currently transported from the river <u>together with congeners that were currently re-emitted from the historic deposit at that site</u>.

Fig 8

Compared with the PCBs currently emitted from the river – that is, the measured airborne congener profile at Coeymans – the measured congener profile at Frost Valley exhibits a considerable increase in the concentrations of the higher congeners. This suggests that, at least in the heat of a summer month, the congeners re-emitted from the historic deposit should dominate the airborne PCB profile at Frost Valley, while the congeners currently transported from the river play a lesser role.

This inference can be evaluated by means of the air transport model. For this purpose we have used the model to estimate the concentrations of airborne congeners transported to the Frost Valley site from the PCBs emitted by the Hudson River as a whole during the August/September study period. This yields a <u>model-based</u> congener profile of the airborne PCBs that were transported to Frost Valley from the river, averaged over the same period in which the measured profile was obtained at that site.

These two profiles are shown in Figure 9, which indicates that the model-based concentration of airborne PCBs at the Frost Valley site is considerably smaller than the measured concentration. The total PCB concentration predicted by the model is 256 picograms per cubic meter, while the measured concentration is 1,740 picograms per cubic meter; thus, <u>current</u> transport from the Hudson River accounts for only 15% of the measured total PCB concentration at Frost Valley.

In sum, it appears that the airborne PCB concentration measured at Frost Valley is largely due to PCB congeners that have followed a complex route: emitted by the river, they were first transported in the air from the Hudson River to Frost Valley; then they were deposited at this watershed site, accumulating over the years since the river was first contaminated; finally – at least in the summer heat of August/September 1998 – they were once again emitted into the air.

Although the total PCB concentration currently transported from the river to Frost Valley represents 15% of the total PCB concentration measured at that site, the corresponding relationship among the separate congeners varies considerably from this average. This is shown in Figure 10, which is a congener-by-congener plot of model-predicted congener concentration, expressed as percent of the measured concentration. In the lower congener group (BZ1-70) this value varies widely from 2% to 78% of the measured concentration. The modeled percentage of the congeners above BZ70 is quite uniformly below 10% of the measured concentration, except for a few outliers in the uppermost range (where there may be inherent inaccuracies due to the low absolute concentrations).

These results indicate that, of the total measured airborne congener concentration at Frost Valley, more than 90% of the high congener group (BZ99 and above) are <u>not</u> currently transported from the Hudson River, but represent PCBs re-emitted from the historic deposit. This is in keeping with the earlier evidence that

fig 9

fig 10

congeners above this number are preferentially deposited at Frost Valley and hence chiefly responsible for the historic deposit. The behavior of the congener group below BZ70 is also in keeping with the earlier evidence that this group tends to remain airborne en route and at the Frost Valley site itself.

B. The Impact of Airborne Hudson River PCBs on the Watershed Basins and Reservoirs:

The overall New York City watershed system consists of six reservoirs and their associated basins in the Delaware/Catskill system west of the Hudson River and 13 older, more closely grouped, reservoirs in the Croton/Kensico system east of the river. Based on the foregoing results, we can regard the river as a source of airborne PCBs, which, depending on weather conditions, may be deposited on each of the watershed system's components. In order to assess the extent of this process, we have used the air transport model to estimate the degree to which each of the system's reservoirs and watershed basins was exposed to airborne PCBs emitted by the Hudson River during the August 20 to September 25, 1998, test period.

The HYSPLIT/TRANSCO model is designed to track airborne PCB congeners from their emission at geographically localized sources, through the intervening atmosphere, to geographically localized receptors (both specified by latitude and longitude). In what follows, the sources, receptors and the types of data that the model generates regarding each of the source/receptor relationships that link the river to the watershed are characterized. Further details regarding model operations are provided in the Appendix.

1. Components of the air transport model:

a. Sources: These are defined as successive 10-mile sectors of the Hudson River from Glens Falls to the New York Harbor. Each sector is defined by its total area and the latitude and longitude of its centroid point. There are a total of 21 centroid source points; all of the PCBs emitted from a given section are assumed to be emitted at its centroid point. (In some sectors, where the model required greater geographic resolution, several additional source points were included, bringing the total to 35.) For convenience the sectors are grouped according to their position into three river sections: upper (Glens Falls to Troy); middle (Troy to West Point); and lower (West Point to the Harbor).

b. Receptors: In the Delaware/Catskill part of the watershed each of the six reservoirs and their associated basins serve as receptors. The areas of each reservoir and each basin were disaggregated into a group of polygons that best encompasses their natural boundaries. These polygon-based areas serve as receptors in the model operations. They are necessarily slightly smaller than the natural areas of the reservoirs and basins. However, in computing the total deposition, the computer-estimated deposition flux (i.e., the amount deposited per square meter) is multiplied by the receptor's natural area. In the Croton/Kensico part of the watershed, the more numerous reservoirs are not assigned to individual basins. Here the receptors are defined as the 13 reservoirs and the East and West sections of the total basin. Hence, there are a total of 15 receptors in this watershed. (7)

c. Model-generated data: Model runs were carried out to estimate the transport of each of eight representative PCB congeners from each of the 35 source points to each of the 27 receptors. These runs generated data in the form of air transport coefficients – that is, the fraction of a unit amount of emission at the source that is received at the receptor. Then TRANSCO was used to take into account the actual rates of emission of all of the PCB congeners, using an interpolation algorithm based on the results obtained with the eight representative ones. Also incorporated in TRANSCO are algorithms that multiplied each source/receptor air transport coefficient by the appropriate PCB emission rates, congener by congener, at the sources.

The overall results are expressed in the following forms at each receptor:

i) Deposition flux: picograms of PCB congeners deposited per day per square meter of receptor;

ii) Deposition: total picograms of PCB congeners deposited per day on the natural receptor area;

iii) Airborne concentration: picograms of PCB congener per cubic meter of air at the receptor's centroid point, 10 meters above ground level.

For the sake of simplicity, these data, generated for each of the source/receptor couples and each of the emitted congeners, have been aggregated. The sources have been aggregated into the upper, middle and lower sections of the river and their sum; for certain purposes, the separate congeners have been aggregated into total PCBs.

2. Results:

a. Source-receptor relationships:

The amount of airborne PCB emitted by the Hudson River that is received by a receptor is governed by the rate of emissions at the source, the source-receptor distance, weather conditions (especially wind velocity and direction), and the geographic relations among sources, receptors, and the wind direction. The estimated PCB emission rates for successive 10-mile sectors of the river are shown in Figure 11. The rates, in grams of PCB emitted per day, vary from sector to sector depending on

fig 11

the PCB concentration in the river water and the area of the10-mile sector. Of the total PCB emissions from the river, 1,200 grams per day, 30% is due to the upper section, 42% to the middle section, and 27% to the lower section.

As shown in Figure 11, the relative impact of the three river sections on the deposition flux at the receptors is clearly influenced by the source/receptor orientation and distance. Thus, three of the four northern-most receptors – the Cannonsville and Pepacton basins and the Schoharie reservoir – receive about half or more of their deposited PCB from the upper (northern) section of the river and the rest from the middle section. The fourth northern receptor, the Schoharie basin, receives two-thirds of its deposits from the middle river, reflecting its closeness to that section. The southern-most receptors, the Neversink and Rondout reservoirs and basins, receive more than three-fourths of their PCB deposition from the middle section, to which they are closest. Similarly, the Croton receptors, which are some 40 kilometers to the south, are distinguished by a considerable contribution from the lower section of the river, and relatively little from the upper section. The Kensico reservoir, the southern-most receptor in the system, receives more than half its deposition flux from the lower section. This reflects the reservoir's proximity to the river and the relatively high rates of PCB emission from the two nearest 10-mile river sectors.

b. <u>The role of source-receptor distance</u>:

Several processes that occur during the air transport process result in a sharp, exponential reduction in deposition at the receptor with increasing source-receptor distance. These include dispersion, diffusion, deposition and destruction en route. This effect is illustrated by Figure 12A, which relates the airborne PCB concentration at the 13 Croton/Kensico reservoirs and the six Delaware/Catskill reservoirs (plus the Frost Valley measurement site) to their distance from the closest point of the Hudson River. The PCB concentrations at the reservoirs decline with distance from the river in keeping with a systematic exponential relationship. Similarly, Figure 12B shows the relation between deposition flux and source/receptor distance at each of the reservoirs. In both cases, apart from two outliers, the relatively high regression coefficients (R^2) indicate that airborne concentration and deposition flux are systematically governed by the expected influence of the physical factors that diminish these parameters exponentially with increasing source/receptor distance.

The Kensico reservoir is a notable exception to this generalization; as an extreme outlier in the regression curves, it has not been included in the calculation of the regression coefficients for the Croton/Kensico receptors. The unusually low values at Kensico may result from limitations inherent in the HYSPLIT model that tend to introduce inaccuracies in relatively short range transport from area sources. In order to counteract this effect, which was expected to influence the model results for the Croton/Kensico receptors, the density of standard source points was increased in the

fig 12a

fig 12b

adjacent part of the river. However, this was not done in the region near Kensico, so that it is likely that some air transport trajectories, especially at high wind speeds, were too narrow to effectively encounter the Kensico receptor site, thereby reducing modeled airborne PCB concentration and deposition. A second reservoir, Cross River, which also has anomalously low values and lies at the southern edge of the main group of Croton/Kensico reservoirs, may be affected by this problem.

It should also be noted that the data in both Figures 12A and 12B do not take into account differences in the rate of PCB emission from the successive sectors of the river. This is most marked in the lower section, where emissions rates are significantly more variable than they are in the upper and middle sections. This may also contribute to the anomalously low deposition flux at the Kensico reservoir, which receives 58% of its PCBs from the lower section of the river, and to the Cross River reservoir anomaly as well.

In sum, the detailed differences among the receptors in both parts of the New York City watershed, with respect to the concentration and deposition of airborne PCBs originating in the Hudson River, reflect the expected relations to the weather pattern and their respective source/receptor distances.

c. <u>The role of geographic orientation to wind speed and direction</u>:

There is a sharp difference between the two divisions of the watersheds with respect to their geographic relation to the Hudson River. The river runs north and south, with the Delaware/Catskill watershed to the west and the Croton/Kensico watershed to the east. The significance of this orientation is evident from Figures 13A and 13B, which represent the daily wind direction and velocity during the August/ September 1998 test period in each of the watersheds. (These data are extracted from the NOAA weather model provided with HYSPLIT and therefore governed the outcome of the air transport processes. Wind direction is unadjusted from the model's polar stereographic projection.) The preponderant wind movement is eastward.

The effectiveness of the advection to which the initial PCB emissions are subjected by the wind – that is, the efficiency with which the wind carries the PCBs to the receptor – depends on both the wind speed and wind direction. It will be recalled that the air transport model follows the fate of a unit amount of PCB from a <u>point</u> of emission. During air transport this unit amount rapidly spreads into an ever-increasing volume due to advection, dispersion, vertical mixing and diffusion. As a result, the PCB concentration of the emitted unit amount (e.g., picograms of PCB per cubic meter of air) decreases with time, as does the amount of PCB available for deposition on the receptor. For this reason, if the wind speed is high, so that the source/receptor distance is traversed in a short time, the PCB concentration and the deposition flux at the receptor will be relatively high. As can be seen from Figures 13A and 13B, during fig 13a-b

the study period the average Eastward wind speed (7.5 kilometers per hour at East Croton) was considerably greater than the average Westward wind speed (2.7 kilometers per hour at East Croton). Accordingly, the travel time between the river and the receptors was much shorter for those in the Croton/Kensico watershed than for those in the Delaware/Catskill watershed. Thus, as shown in Figure 12B, at the same source/receptor distance, the Croton/Kensico receptors receive correspondingly greater airborne PCB concentrations and deposition flux. Moreover, at East Croton, Eastward winds were 3.5 times more frequent than Westward winds, generating a greater average concentration of airborne PCBs.

Thus, receptors east of the river are expected to experience much more intense exposure than receptors to the west of the river from an equal rate of PCB emission at the river during the study period. This expectation is borne out by the results shown in Figures 14A and 14B, which present the model-predicted airborne concentrations and deposition flux at each of the watershed receptors that result from air transport of PCBs emitted from the entire river. Both forms of exposure are far more intense in the Croton/Kensico watershed than they are in the Delaware/Catskill watershed. The diminishing intensity of exposure with the receptors' distance from the river is evident, especially in the latter due to the relatively long distances involved.

It should be noted that these airborne concentrations represent only the PCBs currently transported to the watershed from the Hudson River. As shown earlier for the Frost Valley site, a much larger source of airborne PCBs are the historically deposited congeners that are re-emitted in the high summer temperatures. If this holds also true for the Croton/Kensico watershed, then the actual concentration of airborne PCBs in area may be even higher than the modeled estimates.

d. Total amount of PCBs deposited on the watershed:

From the areas of the receptors and their respective deposition flux, we can estimate the total amount of PCBs deposited on them during each day of the test period. The results are shown in Table I. The total watershed, including deposition on each reservoir and the associated basin, receives a total deposition of 8.26 grams of PCB per day due to emissions from the Hudson River. It is of interest to compare this level of exposure with the total amount of PCBs emitted by the river. As indicated earlier, in the August/September 1998 test period the river emitted a total of 1,200 grams of PCBs per day, of which about 0.7% was deposited on the watershed.

3. Environmental impact:

Because of their environmental effects and hazards to health, the new production and general use of PCBs was banned in the United States in 1977. Based on animal studies and some studies of human health effects, the U.S. National

fig 14a

fig 14b

table I

Toxicology Program has classified PCBs as "reasonably anticipated to be a human carcinogen." (8) Other health effects that may occur at environmental levels of PCBs include neurotoxicity, behavioral changes, liver damage, and injuries to the thyroid gland. In wildlife, such as fish, fish-eating birds and polar bears, environmental exposure has resulted in reproductive failure and other signs of endocrine disruption.

a. Aquatic impact:

EPA and state agencies have established "Ambient Water Quality Criteria" regarding the ingestion of water and organisms (fish and shellfish) in surface waters, including reservoirs. The present EPA criterion for the ingestion of organisms is a PCB concentration in the water of $4.5x10^{-5}$ micrograms per liter, which is equivalent to 45 picograms per liter. (4) (Due to bioaccumulation fish living in such water will have a much higher PCB concentration than the water.) This regulation is intended to limit the lifetime cancer risk from eating such fish to one per million – the so-called "acceptable" level, according to EPA. Recently, EPA has proposed to revise this regulation for "ingestion of water and organisms or [*emphasis added*] ingestion of water" to $1.7x10^{-4}$ micrograms per liter, or 170 picograms per liter. (4) (The risk from ingesting water alone is much less than the risk of eating fish living in that water.) For its part, the New York State Department of Environmental Conservation has issued an ambient water quality criterion based on the ingestion of fish of 0.001 micrograms per liter, or 1000 picograms per liter. (4)

In addition to these criteria for PCB concentration in aquatic environments, EPA has established a "Maximum Contaminant Level" to govern the allowable PCB concentration in drinking water – i.e., water flowing from a tap. The present regulation, established in 1998, is 0.5 micrograms (50,000 picograms of PCB per liter). However, according to EPA, this level "corresponds to a lifetime cancer risk of 10^{-4}" (i.e., one in 10,000). (9) If the regulation were computed to correspond to the "acceptable" lifetime cancer risk as defined by EPA itself – one per million – then the allowable PCB level in drinking water would be 0.005 micrograms per liter, or 5000 picograms of PCB per liter. The New York State drinking water standard is 0.1 micrograms of PCBs per liter, much less stringent than the Federal standard; in comparison, the drinking water standard in New Hampshire is 0.005 micrograms of PCBs per liter. (10)

In sum, the present Federal regulations applicable to the water as it occurs in the New York City reservoirs, based on the EPA-adopted (but not always honored) "acceptable" lifetime cancer risk of one per million, is 45 picograms of PCBs per liter; this risk is almost entirely due to eating fish living in the reservoir. A proposed EPA aquatic criterion that is also applicable to ingestion of the water alone is 170 picograms of PCBs per liter. Regulations directly applicable to drinking water call for a maximum concentration of 50,000 picograms of PCBs per liter. However, if, as would seem proper, this drinking water regulation were based on the EPA one-per-million lifetime cancer risk standard, the regulated maximum would be 5,000 picograms per liter, a standard adopted by New Hampshire.

As an initial step, the environmental impact of the PCB concentrations in the watershed reservoirs that arise from the deposition in them of airborne PCBs emitted by the Hudson River can be compared to these existing regulatory criteria. A full evaluation of the impact would require studies as extensive as those that have been underway in recent years to evaluate the ecological impact of the PCB levels in the Hudson River itself. There, it has been recognized that the large amounts of PCBs dumped into the river from General Electric plants have created a highly concentrated “sink” of PCBs in the sediment in the Thompson Dam pool which has contaminated the downstream river, leading to unacceptable PCB levels in fish and other organisms. For example, based on our analysis of the PCB concentration in the middle and lower sections of the river (see Section B.2.a. above), the average concentration in August/September 1998 was 5,280 picograms of total PCB per liter, clearly well above the existing ambient water quality criteria. Corresponding analyses of the environmental impact of the Hudson River airborne PCBs on the New York City watershed would require similar studies of the effect of the historic deposits of airborne PCBs in the reservoirs and their basins.

b. <u>Direct exposure to airborne PCBs</u>:

People are potentially exposed to airborne PCBs through inhalation. The U.S. EPA has recently made a detailed study of this risk associated with the PCB pollution of the Hudson River north of the Troy dam. (4) We have employed their criteria for assessing the inhalation health risk to people living near the river and inhaling PCB vapor at the concentrations we have determined at Coeymans. The assessment may apply to people living in Troy, Rensselaer, Albany, Castleton, Hudson, and Poughkeepsie, the main centers of population along this stretch of the river, since PCB emissions are generally the same or higher than at Coeymans river section.

The EPA separates PCBs into three “tiers” for cancer risk purposes. The “High Risk and Persistent” category is defined as congeners found in Hudson River fish; these congeners were measured in the air samples taken at Coeymans. They are assigned a “slope factor” of 2 $(\text{mg/kg-day})^{-1}$ which, when multiplied by the estimated lifetime daily dose, yields the risk of developing cancer per 1,000,000 people, the maximum “acceptable” risk according to EPA. (The cancer slope factor is an upper estimate of the carcinogenicity of PCBs.)

The daily lifetime dose of each congener was determined from the mean airborne PCB concentrations over the 28-day study period, and the average volume breathed by a 70 kg person. This led to an exposure of 50,000 picograms per day for “High Risk and Persistent” congeners, corresponding to a dose of 710 picograms per kilogram of body weight per day, or 0.71×10^{-6} milligrams per kilogram per day. Multiplying the dose by the slope factor yields a lifetime cancer risk of 1.42 per 1,000,000 – about equal to the maximum “acceptable” risk according to EPA. Given that the airborne PCB concentrations in the Croton/Kensico area appear to be greater than the concentration at the river (Coeymans), the risk would be correspondingly greater there.

IV. EVALUATION OF RESULTS

This section considers possible uncertainties that might limit the significance of the foregoing results.

A. Evaluation of the PCB Air Transport Model:

Like all such mathematical models, the HYSPLIT/TRANSCO model of PCB air transport represents an effort to reduce an inherently complex real-world process to a set of mathematical statements that can predict the actual outcome of that process – in this case, the amounts of airborne PCBs transported from the Hudson River to designated sites in the New York City watershed system.

A basic question naturally arises: Instead of depending on a model that indirectly estimates the amounts of PCBs at the various watershed sites, why not measure them directly? Such measurements are, of course, useful ways to estimate the local exposure to PCBs at the site. However, they do not in themselves provide information about the source(s) of the exposure – which is an essential element of this project. The HYSPLIT/TRANSCO model can provide such information.

However, a second basic question then arises: How can the reliability of the model be tested? The preferred method of dealing with this situation is to compare the predicted values generated by the model with actual measurements. For example, in an earlier study the HYSPLIT/TRANSCO model was used to predict the amount of dioxin emitted from an inventory of all known U.S. and Canadian sources that gave rise to airborne concentration at specified sites (e.g., dairy farms). The predicted values were compared with actual measurements made at the same time at the same site and found to be reasonably accurate estimates of the actual values (11). This result testifies to the reliability of the HYSPLIT model's basic structure, which is the same whether it is adapted to dioxin or PCBs. HYSPLIT has evolved at NOAA from a relatively simple version in 1982 to version 4 in 1998, progressively incorporating the latest analyses of the relevant atmospheric, chemical and physical processes. HYSPLIT has been validated by real-world data, for example, long-range balloon tracer experiments on the Rabaul volcanic eruption and radioactive fallout from the Chernobyl accident. (12)

In the present case this direct approach to model evaluation was not possible because the sources of PCB emissions are far too numerous and widespread to be completely inventoried; they would need to include, for example, wooded areas such as Frost Valley which – at least in the summer – is a source of airborne PCBs. Nevertheless, within the data described in the preceding section are observations that, taken together, set useful limits to errors that may be inherent in the PCB air transport model. These are summarized below.

B. The Reliability of Model-Estimated PCB Deposition and Airborne Concentration:

On its face, the comparison of the measured concentration of airborne PCBs at Frost Valley with the model-estimated concentrations of PCBs transported to that site from the Hudson River might be regarded as a model validation test. But this would be so only if the Hudson River were the only source affecting Frost Valley. As already noted, there are in fact additional sources that influence the airborne PCB concentration at Frost Valley: certain congeners re-emitted from historic deposits of PCBs transported from the river and, to an unknown extent, “background” PCBs. Nevertheless, as shown in Figure 10, apart from two outliers, in the remaining 77 congeners, the modeled concentrations are all below the measured concentration. Accordingly, if the model does not accurately estimate the real values, it may be more likely to under-estimate them.

C. The Reliability of the Model’s Response to Variations in Parameters That Influence PCB Deposition and Concentration:

Figures 12A and 12B show that the model reliably reflects the distance-modulated effects on PCB air transport. As expected from physical considerations, the model-predicted airborne PCB concentration decreases exponentially with source/receptor distance. In addition, Figure 11 shows that, as expected, at each receptor the relative contributions of PCBs from the three river sections reliably reflect the receptor’s proximity to them.

Figure 5 describes two sets of model-estimated air transport coefficients (ATC) for deposition of airborne PCBs emitted by the Hudson River (at Coeymans) to the Frost Valley site. The model runs involved different time periods – five weeks in August/September 1998 and a one-year period beginning in February 1998 – and hence were affected by very different weather conditions. Nevertheless, the model-generated results exhibited the expected similarities and differences. Thus, because the congeners’ tendency to bind to particles – and hence to deposit – increases with their critical temperature (Tc), as expected the model-estimated increase in deposition flux with increasing BZ number follows a similar course in both tests. The larger increase observed in the one-year test reflects the fact that rainfall is, of course, greater over one year than it is in five weeks, for precipitation greatly enhances particulate deposition. Moreover, both cases show decreases in the airborne concentration ATC of the higher congeners that reflect – as they should – the influence of their preferential deposition.

These examples signify that the air transport model can reliably reflect the expected effect of source-receptor distance and the characteristic properties of the different PCB congeners.

We note that the detailed data on PCB deposition in the individual components of the watershed system are based on modeled air transport only during the five week August/September 1998 period. It is of interest, therefore, to consider how seasonal weather patterns might affect such results over the course of a full year. Seasonal effects due to variations in the PCB concentration in river water (which influences the rate of emission to the air) are unlikely since this concentration during the five-week study period was close to the yearly average for 1998. On the other hand, as noted earlier, we expect that the increased frequency of rain and snow (which facilitate deposition) over the course of a year would increase deposition of the more highly chlorinated congeners. The most significant seasonal differences among receptors are likely to arise out of their east-west orientation towards the Hudson River, due to seasonal patterns of wind direction and speed, factors we found to be important predictors of relative deposition in our five-week runs.

D. The Background Problem:

In a sense, this is perhaps the most distinctive difference between modeling PCBs and otherwise similar toxic pollutants such as dioxin. Because they are so stable and so widely varied in their physical properties, especially in response to ambient temperature, PCBs have become pervasively distributed in the environment. Over the years since they were first manufactured, the sources of PCBs have included, not only the facilities in which they have been produced or used, and disposal sites (intentional or otherwise), but also every square meter of land and surface waters that have received deposits of airborne PCBs. How, then, is it possible to identify the environmental impact of a single source of airborne PCB, such as the Hudson River, even if it is relatively intense compared with the ubiquitous background? In the present project this question applies particularly to the measured PCB concentration at Coeymans, where we have assumed that background makes only a negligible contribution.

The assumption that air concentration measurements taken at the Hudson River represent PCBs emitted from the river is supported by several EPA-sponsored studies. The results suggested that "...the PCBs detected in the air were emanating largely from the Hudson River" and that the river was characterized by an airborne PCB concentration between 1,000 and 2,000 pg/m^3. (4) Thus, the airborne PCB measured at Coeymans, 1760 picograms per cubic meter, is in keeping with these independent estimates and can be regarded as largely due to congeners emitted from the river. Farley cites an airborne PCB concentration measured in a non-urban coastal area (Sandy Hook, NJ) in 1998, sufficiently close to the Hudson River estuary to be regarded as a relevant background value. That concentration, 227 picograms per cubic meter, is 13% of the measured concentration at Coeymans.

V. CONCLUSIONS

Recent studies have shown that most of the PCB in the heavily contaminated Hudson River is emitted into the air – as much as 65% in 1997. (5) Our project has evaluated the exposure of the New York City watershed to this hitherto unexamined airborne source of toxic contamination. An air transport model has been used to track the individual PCB congeners emitted from successive 10-mile sectors of the river to each of the reservoirs and basins that comprise the overall watershed system. The results generated by the model and by analyses of airborne PCBs sampled at a river site (Coeymans) and at a site in the Neversink watershed (Frost Valley) support the following conclusions.

1. The New York City watershed is systematically exposed to airborne PCBs emitted from the Hudson River, thereby expanding the ecological domain affected by this toxic pollutant to an important natural resource beyond the river itself. The airborne PCBs that have been deposited on the watershed, chiefly the more highly chlorinated (and generally more toxic congeners), tend to accumulate there – in vegetation, soil and reservoir sediments. In warm summer temperatures the accumulated PCB congeners vaporize; re-emitted into the air, they give rise to the unusually high airborne PCB concentration measured at Frost Valley in the Neversink watershed: 1740 picograms per cubic meter. Yet, the model predicts a concentration at Frost Valley of only 256 picograms per cubic meter due to PCBs concurrently transported from the Hudson River. Thus, the high airborne PCB concentration in the watershed reflects a long-term accumulation and revolatilization process that has been underway since the Hudson River was first heavily contaminated with PCBs in the 1950s – earlier at much higher rates than at present according to EPA studies.

2. The sequential events that have contaminated the watershed with airborne PCBs emitted from the Hudson River are consistent with the known facts about the physical processes that govern the environmental fate of PCB: the effect of ambient temperature on the volatility and deposition of the different PCB congeners; increased dispersion, and therefore decreased deposition, with distance between the river (the source) and the watershed sites (the receptors); wind speed and direction.

3. The exposures of the different watershed reservoirs and basins to the airborne PCBs emitted from the Hudson River vary considerably. The Croton/Kensico watershed, which lies east of the river, is exposed to particularly large amounts of airborne PCBs from the Hudson River because, compared to the Delaware/Catskill watershed, which is west of the river, it is relatively close to it and – at least during our study period – subject to eastward, more intense, winds. The reservoirs in this watershed, which account for only 21% of the volume of the total system, receive 80% of the total deposition of airborne PCBs transported from the Hudson River to both watersheds. As a result, PCB concentrations in the reservoirs of the Croton/Kensico system may be several times greater than the concentration in the Delaware/Catskill reservoirs.

4. In sum, these results redefine the ecological domain affected by the PCBs

originally discarded into the upper Hudson River. In the river they have led to the formation of a "sink" of heavily contaminated sediment in the pool above the Thompson Island dam, which continues to release unacceptable levels of PCBs into the downstream sections. It now appears that this ecological hazard extends beyond the river itself, for the air transport model predicts that the airborne PCBs emitted from the river and deposited in the watershed may also reach unacceptable levels in the reservoirs. And just as the accumulated PCBs have caused the river to serve as a source of airborne PCBs, so too, the accumulated PCBs in the watershed, for example at Frost Valley, have been re-emitted, accounting for most of the airborne concentration measured at that site. Ironically, it is likely that some of this airborne PCB, carried eastward by the prevailing winds, is redeposited in the river, thereby counteracting to a degree the PCB volatilization that has helped to reduce the PCB level in the river water.

Finally, we note that the existence of this enlarged PCB-contaminated ecological domain is thus far based on an air transport model – an inherently indirect method of assessing PCB deposition and accumulation. Accordingly, this assessment should be confirmed by direct measurements of PCB accumulation in the watershed. This can be done, for example, by measuring the PCB content of reservoir sediments and tree bark (which has been shown to accumulate airborne PCBs (13)); in both cases dating techniques can be used to delineate the history of PCB accumulation (in sediments, by serial analysis of layers; in tree bark, by comparative analysis of bark from trees of different ages).

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