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Session Summary Report

Atmospheric Levels, Transport and Deposition- EM8

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Introduction

This session is comprised of 18 presentations on a wide variety of topics related to levels, sources, transport and fate of a number of POPs in the global atmosphere. The session has been divided into a platform session comprised of seven oral presentations and poster sessions containing the balance or eleven presentations. POPs of particular interest in the eighteen presentations include PCDD/F, PCB, co-planar PCB, PBDE, PCN and a number of organochlorine pesticides. Ambient measurements for one or more of these POPs categories are reported for eleven nations (number of papers) participating in this session: Canada (3), USA (2), Italy (2), Spain (1), Korea (2), Japan (1), Taiwan (1), Poland (3), Denmark (1), Portugal (1) and Brazil (1). A wide-variety of established and emerging topics is covered by a truly international team of experts.

PCDD/F and PCB- Atmospheric Levels, Trends and Sources

The majority of the offerings on this topic present data on POPs in the atmosphere of the participating nation. **[Paper 228]** Jorgen Vikelsoe and Helle Vibeke Andersen report on ambient PCDD/F in and around metropolitan Copenhagen Denmark. These data were collected as part of the Danish Dioxin Monitoring Program for the purpose of establishing background levels, examining differences in comparison of urban, rural, and residential exposures as well as the influences from local sources and long-range transport. Minimum PCDD/F concentrations were observed in summer months (June) and maximum levels observed in the winter months of February and March. Ambient concentrations at the urban Copenhagen site are comparable to levels observed at a rural site in Fredensborg approximately 30 km north of Copenhagen. These data suggest long-range transport to the rural site as a significant factor contributing to levels observed at this location. The highest concentrations were observed at Gundsomagle, a rural residential village situated 30 km west of Copenhagen, in winter months coincident with the heating season. This observation in combination with high PAH levels suggests domestic heating with wood stoves as the major source of PCDD/F emissions on a localized basis. **[Paper 418]** Gustems Lluis and his colleagues report ten years of PCDD/F data for 29 sampling stations located throughout Catalonia, Spain. The highest concentrations of PCDD/F were observed in industrial locations ranging from 5-1200 fg I-TEQ/m^3 with a mean concentration of 140 fg I-TEQ/m^3. Levels found in urban and suburban locations were lower ranging from 8-620 fg I-TEQ/m^3 (mean = 110 fg I-TEQ/m^3) and 7-1200 fg I-TEQ/m^3 (mean = 120 fg I-TEQ/m^3), respectively. It was felt that the urban sites were impacted most significantly by emissions from vehicular traffic at these locations. PCDD/F concentrations for rural and background settings in Catalonia were found to be much lower than observed at urban and industrialized locations. Rural sites ranged from 5-45 fg I-TEQ/m^3 (mean = 28) and background concentrations ranged from 8-28 fg I-TEQ/m^3. Comparable PCDD/F concentrations were observed in comparison of data collected using both PM10 and TSP particulate sampling systems. **[Paper 152]** Tzu-Yi Lee and his colleagues present results for a nationwide survey of PCDD/F in ambient air in Taiwan during the period 2002-03. Results are reported for 17 samples collected each of eight monthly sampling events using a 13 site network covering the period August 2002-November 2003. The highest mean I-TEQ concentrations were observed in May 2003 and the lowest in July 2003. Mean concentrations ranged from 0.062-0.130 pg I-TEQ/m^3. A downward trend was noted in comparison of these data to data collected during 1999. The authors attribute the lower ambient levels to initiatives taken by U.S. EPA to reduce emissions from stationary com-

bustion sources and in particular 19 municipal solid waste incinerators (MSWI) operating within Taiwan. **[Paper 154]** Miguel Coutinho and colleagues focus on PCDD/F levels in ambient air in the industrialized regions of Oporto and Lisbon Portugal. Of particular concern in the Oporto region were contributions from combustion processes such as an MSW incinerator in operation since 1998. This presentation examines data collected during the period June 1998- February 2004. Concentrations measured in Lisbon were observed to be comparable to those found in other rural and non-contaminated areas around the globe. The Oporto levels, conversely, were approximately four times higher than what was found in the Lisbon region. The majority of the Oporto samples (77%) ranged from 40-400 fg I-TEQ/m^3. As is the case in many other regions of the globe, winter concentrations were dramatically higher than summer levels (3-4 times in Oporto). Again, the major seasonal contribution to the higher winter levels was believed to be residential wood burning. Hierarchical cluster analyses of the PCDD/F data including homologue profiles indicated that a hospital waste incinerator and not the MSW incinerator was contributing to ambient levels observed in the Oporto region prior to winter 2000-01. Shutdown of the hospital waste incinerator in early 2001 resulted in a redistribution of homologues (increase in tetra-CDF species) and an apparent decrease in regional levels of PCDD/F. **[Paper 62]** Yoon Ki Min and colleagues from Gyeonggi-do Institute of Health and the Environment examined atmospheric levels of PCDD/F and PCBs in the Gyeonggi-do region of Korea. This region of Korea represents 10% of the land area of Korea, contains Seoul the Korean capital, as well as a population of 10 million (21% of the country's population). Additionally, this region of the country contains an estimated 12,700 sources of air pollution. PCDD/F data are reported for the period August 2001-December 2003. Average concentrations are reported for each of six sites in the network. When data were organized by season of collection, it was observed that the highest concentrations occurred in winter months followed by spring > summer > autumn. PCBs measurements commenced in February 2003 at each of the six sites. The average PCBs TEQ was 0.024 WHO-TEQ/m^3. The highest PCB concentrations were observed at the Siheung and Ansan sites; 0.044 and 0.043 WHO-TEQ/m^3, respectively. **[Paper 197]** David Cleverly and colleagues from the United States report PCDD/F and PCBs levels for calendar year 2001 at NDAMN sites in the continental United States. This presentation provides an update on data reported previously for calendar years 1999 and 2000 at prior meetings. Annual mean PCDD/F concentrations measured at 22 rural sites in 2001 ranged from 2-28 fg/m^3 (WHO) TEQ. The overall mean for the 22 sites was 12 fg/m^3 WHO-TEQ. Mean annual PCB TEQs ranged from 0.15-9 fg/m^3 with an overall mean of 1 fg/m^3 WHO-TEQ. PCDD/F levels at remote sites were approximately one order of magnitude lower than levels reported for the rural sites. The overall mean for the eight remote sites was 1.1 fg/m^3 WHO-TEQ. PCBs were reported to be five times lower at remote sites than was observed at rural sites. The overall mean for PCBs at the eight remote sites was 0.23 fg/m^3 WHO-TEQ. PCBs concentrations at the remote sites were found to be generally higher in summer months in comparison to winter months. This trend was attributed to increased volatilization of PCBs from soils during warmer times of the year. **[Paper 205]** Kyoung-Soo Kim from the Institute of Environmental Chemistry in Jeonju, South Korea and Shigeki Masunaga from the Yokohama National University in Japan collaborated on a study that examined the levels and origins of PCBs in the ambient air of Yokohama City, Japan. Statistical treatment of the data employing principal component analysis indicated that Kanechlor products and combustion sources were the major sources of PCBs.

PCDD/F and PCB -- Fate and Transport in the Atmosphere- Deposition

[Paper 416] Marcia de Souza Pereira and her colleagues report on deposition rates for PCDD/F and PCB in Volta Redonda City, a highly industrialized portion of the State of Rio de Janeiro Brazil. Deposition samples displayed a thermal profile for PCDD/F with predominance of furans over dioxins. Such a profile is often indicative of stationary combustion sources. Use of *Tillandsia usneoides*, an epiphytic bromeliad, as a bio-monitor was also examined as part of this study. Based upon results it was found to be an excellent, reliable, and low-cost bio-monitor for airborne persistent organochlorine compounds in tropical climates such as are found in Brazil. Deposition rates

are reported for each of four sites in the network. Deposition rates for both soils and bio-monitor samples deployed at each of the sites are reported. These rates include PCDD/F and PCB WHO-TEQ in units of pg m^{-2} day^{-1} for soils and ng/kg for the bio-monitor. **[Paper 550]** Sean Backus and his cohorts from Environment Canada report on concentrations of PCDD/F in wet deposition samples collected at a site in Burlington, Ontario, Canada. The site is situated in close proximity to industries in Hamilton, Ontario and is adjacent to a major highway serving southern Ontario. Little variability in wet deposition rates or fluxes was observed for PCDD/F in comparison of six monthly samples collected during the period of June-November 2003. A mean rate of 5.3 pg m^{-2} day^{-1} was observed for Cl_4-Cl_8 PCDD/F (0.62 pg WHO-TEQ m^{-2} day^{-1}). The maximum rate observed at the site of 1.2 pg m^{-2} day^{-1} occurred during the November 2003 sampling event. The total flux showed little seasonal variation during the six month period examined. The ratio of dioxins to furans did not vary during the period either; a mean value of 2.8 was observed. 2,3,4,7,8-PeCDF was found to represent the largest contribution by a single isomer to the TEQ (20-30%). No seasonal differences were observed in comparison of PCDD/F congener profiles for the study period.

Gabriele Matteucci and Paolo Rossini from Istituto di Ricerca Gruppo CSA in Rimini, Italy and their cohorts provide two contributions to the session associated with deposition of POPs to the Venice Lagoon and soils of the industrial district of Porto Marghera, Italy. Prior studies had indicated that the highest levels of PCDD/F and PCB in the Venetian environment are found in the Porto Marghera industrial district situated directly west of Venice. Preliminary analyses conducted in 1999 suggested that atmospheric deposition accounted for as much as one-quarter of all PCDD/F inputs to the lagoon. This is equivalent to 12 grams or 400 mg WHO-TEQ PCDD/F annually. **[Paper 495]** The purpose of the current study reported here was to improve upon the understanding of profiles of PCDD/F and PCBs in soils of the region by comparison of fluxes derived from atmospheric deposition in concert with soil and sediment measurements. Examination of the PCDD/F data indicated a strong association of levels with the industrial district. An exponential decay of PCDD/F concentrations was observed with increasing distances from the industrial region. PCBs, conversely did not display this same decay pattern, suggesting multiple sources. PCDD/F and PCBs concentrations in undisturbed surficial soils were 1-2 orders of magnitude higher than would result from atmospheric deposition based upon the most recent field measurements. The authors attribute this to a decline in emissions in recent years attributable to a partial decline in industry coupled with new Italian government legislation on air emissions and use of pollution abatement systems. **[Paper 487]** The second contribution by these authors examines total deposition fluxes and atmospheric loadings of POPs in the Porto Marghera industrial district. Data were collected monthly employing bulk deposition samples from a seven station network. It was observed that PCDD/F levels in soils attributable to emissions from the industrial district occurred at distances greater than 8 km from the district. Annual atmospheric loadings were reported for a variety of POPs as follows: PCDD/F = 12 g, PCBs = 540 g, HCB = 100 g and PAHs = 100 kg. These atmospheric loadings equated to 280-440 mg as TEQ. Despite the observation that deposition rates for PCBs and HCB had decreased since the 1998-99 measurements atmospheric deposition of POPs to the Porto Marghera and Venice Lagoon were still viewed as significant.

Pine Needles as Passive Monitors for PCDD/F, PCB and PCN

The use of pine needles as a passive collection device for atmospheric POPs in Poland is the focus of three presentations prepared by Anna Orlikowska and Ilona Bochentin and their colleagues from the University of Gdansk in Gdansk Poland in collaboration with Barbara Wyrzykowska and her colleagues from the National Institute of Advanced Industrial Science and Technology (AIST) in Tsukuba Japan. **[Paper 400]** The first of these presentations employs pine needles as bio-monitors for PCDD/F and PCB at 11 sites throughout Poland. One year old pine needles (*Pinus silvestris*) were collected at each of the sites during October 2002. Total PCDD concentrations ranged from 13-48 pg/g wet weight, and total PCDF concentrations ranged from 21-77 pg/g wet weight. Elevated concentrations of PCDD/F were observed at sites in south Poland believed to be attributable

to mining, hard coal, and metallurgy sources in this region. Homologue profiles for PCDD/F were comparable across the 11 site network. Coplanar PCBs concentrations in these same samples ranged from 0.14-1.54 pg TEQ/g wet weight. The highest concentrations were found in samples from industrialized and heavily populated regions of the country. The lowest concentrations were found in samples from the eastern and western parts of the country. The authors attribute elevated concentrations to the following sources: former PCBs production sites, PCBs in waste disposal, mining, and other industries. Total PCBs ranged from 2.8-50 ng/g wet weight. The highest concentrations were observed in the vicinity of former production sites for technical PCBs (Chlorofen and Tarnol) manufactured in Poland. Former Chlorofen production sites in southern Poland were identified as the major source of these compounds in that region. This observation was based in part on the high abundance of highly chlorinated PCBs (six to eight chlorines) in the pine needle samples collected in the southern region. These highly chlorinated homologues are characteristic of the Chlorofen composition. PCBs concentrations in pine needles from three rural sites examined were almost ten times lower than concentrations found in the other region of the country.

[Paper 405] The second offering by these authors reexamines the pine needle data for PCDD/F, PCBs and also includes PCN. Soil sample data are also included in this presentation. PCBs in soils ranged from 0.61-8.6 ng/g dry weight. These concentrations were significantly lower than concentrations observed in pine needles. Homologue group patterns were, however, similar to those found in pine needles and suggested the same sources of fugitive PCBs emissions. **[Paper 404]** The third offering by these same authors focuses exclusively on the distribution of PCN in the pine needle samples as well as the likely origin of this class of POPs in the Polish environment. PCN concentrations in the 11 sample set of pine needles ranged from 165-925 pg/g wet weight. Interestingly enough, the highest concentrations of PCN were observed in the samples from densely populated and industrialized regions of Poland. Samples believed to be influenced by their proximity to sites of former manufacture and/or use of Chlorofen also contained elevated concentrations of PCN. The authors note that PCN are a common impurity in technical grade Chlorofen as their presence is directly attributable to the manufacturing process. The most dominant PCN homologues in the majority of the samples were tri and tetrachlorinated naphthalenes. These homologue groups are predominant in many PCB technical products such as a number of Halowaxes, Aroclors, Phenoclors, Chlorofens, and Kanechlors. For example, Chlorofen PCB technical mixtures characterized by a predominance of the octachlorinated PCN homologue group (represents 98% of PCN in the mixture) were produced and used in Poland. This homologue group represented a significant contribution to PCN found in Polish pine needle samples. In one sample the octachlorinated PCN contribution was > 34% of the total PCN measured. This homologue group is found in the greatest concentrations in the higher molecular weight PCB technical mixtures such as Halowax 1051, Aroclor 1260 and 1262, and Kanechlor 600.

PBDEs- Transport and Fate

[Paper 196] Archil Zarnadze and Lisa Totten from Rutgers University in New Brunswick, New Jersey provide further insight on the transport and fate of PBDEs in the air and water of the Hudson River Estuary. This presentation makes use of the reanalysis of archived samples of ambient air collected at three sites in close proximity to the Hudson River Estuary. Samples from two of these sites New Brunswick NJ and Jersey City NJ are presented here. PBDE congeners of interest included BDE 47, 99,100,153,154 and 190. BDE 190 was not detected in any of the samples examined. PBDE concentrations present in particulate and gas phase samples collected at the two sites were comparable. The authors focused the majority of their discussion on the results from analyses of 26-27 samples collected at the Jersey City site (Liberty Science Center) during calendar year 2000. No seasonal trends were noted in examination of PBDEs present in the particulate phase. Conversely, the majority of the PBDEs present in the gas phase samples increased in concentration during the summer months and decreased in concentration during winter months. The data suggest that PBDEs enter the atmosphere via passive volatilization from PBDE-containing products such as

foams and treated fabrics and less likely associated with active industrial emissions. The most common BDE isomer is BDE 47, which is present in the highest concentrations in both the gas and particulate phases. PBDE totals representing gas and particle phases combined at the Jersey City Site averaged 22 pg/m^3. PCB levels in these same samples averaged 1200 pg/m^3. The authors view these PBDEs concentrations in the atmosphere to be significant particularly in comparison to levels measured at remote sites around the Great Lakes, which were as much as four times lower than reported for the New Jersey sites.

POPs (HCH, PCB, Chlordane and Endosulfan) in the Arctic Atmosphere -- Transport and Fate

Haley Hung from Environment Canada in Toronto and her Canadian colleagues offer two presentations on the topic of POPs in the atmosphere of the Canadian Arctic. **[Paper 121]** The first of these presentations examines spatial variations in the seasonality of a number of organochlorine pesticides in the Arctic atmosphere. The data set examined consisted of weekly air samples from the NCP program collected at four sites in the Canadian Arctic. Vapor concentrations of three organochlorine (OC) pesticides ã-HCH, *t*-chlordane and endosulfan I were used. Elevated vapor concentrations of these compounds measured at the Alert site during the period 1993-1999 were observed before and after the warmest time of the year. Many other OC compounds also displayed elevated concentrations in the months of April and May at the Alert, Tagish, and Dunai sites. These spring peaks or maxima were not observed for transformation/metabolites of parent pesticides, however. These compounds followed seasonal temperature patterns and were highest during the warmer summer months. The authors identified a number of factors likely responsible for the spring maxima observed for parent OC compounds in the Arctic atmosphere. These were as follows: (1) application of pesticides during the spring time, (2) springtime re-volatilization of pesticides trapped in snow cover as snow melts, and (3) scavenging by forests en-route to the Arctic associated with the growing season. The wax-like surface of new leaves would act as a passive collection media for sorption of semi-volatile compounds such as OC pesticides (see presentations in this session on use of pine needles and other plants as bio-monitors or passive sampling devices). **[Paper 82]** In this second paper, Hung et al. examine seasonally averaged vapor phase or gaseous concentrations of á- and ã-HCH and a variety of PCB congeners measured in the Arctic during the period 1993-1999. Nine PCB isomers were examined including PCB 28, 31, 52, 101, 105, 118, 138, 153, and 180. PCB 156 was not detected in 96% of the samples and accordingly was not used in the data analyses. These ambient concentration data were compared to North American surface air temperatures and other indices indicative of Pacific North American (PNA) atmospheric circulation patterns for the same time period. In this manner, the authors examined the influence of climate variations in North America on the long-range transport of OC compounds to the Canadian Arctic. No correlations were found between atmospheric concentrations and the PNA index in winter and fall months. Statistically significant correlations (Spearman correlations at 90% confidence level), however, were found during spring months between the PNA index and air concentrations of ã-HCH and a number of PCB isomers (PCB 28, 31, 52, 101, 153, and 180). These results imply that higher than normal surface air temperatures (SAT) in North America enhances revolatilization of POPs such as ã-HCH and PCBs from existing reservoirs where these compounds have accumulated previously.