12 per mil enriched in C-12 compared to normal marine inorganic carbon. Petrochemical operations release wastes which are enriched in C-12. Both of these types of waste can be traced in the marine environment by using C-13/C-12 measurements. The extent of organic waste clean-up operations can be determined by monitoring the C-13/C-12 ratio of the remaining organic matter in the final effluent.

11. INHIBITION OF OXIDATION OF SULFUR DIOXIDE DURING ALKALINE SCRUBBING.
Paul Counterman and Elmer R. Altwicker, Bio-Environmental Engineering Division, Rensselaer Polytechnic Institute, Troy, New York 12181.

The inhibition of the oxide ion of sulfur dioxide during alkaline scrubbing is desirable from the standpoint of pollution control and economics. The aim of this research is to study the oxidation in a system that may permit translation of the data to industrial absorption systems such as packed columns. The experimental system used consisted of a continuously stirred batch reactor into which gas stream consisting of 88.9% nitrogen, 9.8% oxygen and 1.3% sulfur dioxide was continuously diffused. Sulfite and sulfate concentrations and SO_2 removal efficiency were measured as a function of time. The system parameters studied were: inhibitor-type, inhibitor concentration, catalyst, pH, and time. Benzyl alcohol (2%), phenol (.005%), and hydroquinone (.001%) were all found to be effective inhibitors for contact times as long as 30 minutes. Evidence would indicate that the inhibitor is consumed during oxidation.

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PCB'S I - EVIDENCE FOR UBIQUITY

12. POLYCHLORINATED BIPHENYL (PCB) IDENTIFICATION IN MARINE ARCTIC AND SUBARCTIC FOOD CHAINS. Gerard M. Bowes (1) and Charles J. Jonkel (2). (1) Toxic Chemicals Section, Canadian Wildlife Service, 6 Beechwood Ave., Ottawa, Ontario; (2) Canadian Wildlife Service, Eastern Region, 2721 Highway 31, Ottawa, Ontario. Canada.

Analysis of biological samples from Arctic and Subarctic marine food chains revealed gas chromatographic patterns similar to those of the polychlorinated biphenyls (PCB). Samples were taken from polar bears, seals and fish. Zooplankton, and possibly phytoplankton, analyses also will be reported. Geographical locations represented by the data extend across North America from Alaska to Baffin Island, and down into Hudson Bay. Tissues analysed included brain, liver, meat, and fat. Samples were extracted with hexane after having been ground with sodium sulfate or digested in glacial acetic-perchloric acid. Column material employed for extract clean-up included both Florisil, deactivated 10%, and Celite-fuming sulfuric acid. Quantitation was done on 5% SP-2401(fluorosilicone) on 100-120 mesh Supelcoport. Confirmatory techniques included use of the GC alkaline pre-column, conversion of PCB to decachlorobiphenyl, and silica gel column separation of the PCB and chlorinated pesticides. Electron-capture GC indicates the PCB concentration in polar bears to be greater than the combined DDT and DDE. A striking feature is that the GC PCB pattern in bears from all geographical locations sampled to date, is similar.

13. INSECTICIDES, POLYCHLORINATED BIPHENYLS AND MERCURY IN WILD CORMORANTS, PELICANS, THEIR EGGS, FOOD AND ENVIRONMENT. Yvonne A. Greichus, Algirdas Greichus, Royce J. Emerick, Experiment Station Biochemistry Department and Entomology-Zoology Department, South Dakota State University, Brookings, South Dakota 57006.

A study of the levels and distribution of organochlorine insecticides, polychlorinated biphenyls (PCB's) and mercury in water, bottom sediments, fish and fish-eating birds from the Lake Poinsett, South Dakota ecosystem was conducted during the summers of 1970 and 1971. Levels of all three compounds increased in higher trophic levels with insecticides concentrating most rapidly and mercury least rapidly. Average levels in bodies of Double-crested Cormorants were 10.0, 6.6 and .64 parts per million and in bodies of White Pelicans were 12.3, 2.3 and .29 ppm for insecticides, PCB's and mercury respectively. Other tissues examined for these compounds included brain, muscle, kidney, liver, fat and eggs.

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Procedures used in the purification, identification and quantitation of insecticides and PCB's included column, gas-liquid and thin-layer chromatography and saponification and oxidation of samples. The presence of PCB's in pelicans, cormorants and their eggs was confirmed with mass-spectrometry. A procedure for the removal of all insecticides from the PCB's was employed prior to the mass-spectrometry analysis.

14. MOVEMENT OF PCB'S THROUGH THE CHESTER RIVER ESTUARY. J. B. Taylor and T. O. Munson, Westinghouse Ocean Research Laboratory, P.O. Box 1771, Annapolis, Maryland 21404.

As part of a multi-disciplinary study (jointly funded by the State of Maryland and the Westinghouse Electric Corporation) of the Chester River Estuary (part of the Upper Chesapeake Bay), the authors analysed bottom sediments, suspended sediments, water and biological tissues for PCB's and "hard" chlorinated pesticide residues. The levels of pesticides observed were relatively low for most of the year although some "contaminant" peaks were observed which could easily be mistaken for pesticides or PCB's. The PCB contamination (of the Aroclor 1232-42 type) was low compared to the part-per-million levels observed by others in the lower Chesapeake Bay but was high enough to indicate inputs other than general atmospheric fallout. Information from the hydrological, meteorological, and geological parts of the program was used to estimate the possible rates and routes of the chlorinated hydrocarbons through the system.

15. PCB CONTAMINATION OF THE AQUATIC ENVIRONMENT IN ONTARIO, O.W.Berg, P.L.Dilmady and G.A.V.Rees, Ministry of the Environment, Laboratory Branch, Box 213, Rexdale, Ontario, Canada.

Sporadic analyses of samples from the aquatic environment have shown that PCB's are universal pollutants. Almost without exception the contaminant was of the Aroclor 1254 type. The approximate levels were as follows: effluents from sewage treatment plants-0.001-0.1 ppm, river sediments-up to 0.6 ppm, fish-up to 20 ppm and seagulls-up to 1500 ppm in oil.

In order to gain more systematic type of information, a large scale survey was undertaken. Four different types of aqueous systems were studied: 1. industrialised "impounded system", 2. industrialized "dynamic system", 3. natural "impounded system" - a clean lake receiving no waste and 4. natural "dynamic system". Data concerned with the analysis of water, bottom sediments and fish are presented and discussed.

The analytical techniques - separation of PCB's from other chlorinated materials and the determination of PCB's in terms of the fully chlorinated derivatives-decachloro biphenyl are discussed as well.

16. DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN THE AQUATIC ENVIRONMENT. Marvin L. Yates, Norman R. Foltz, and Hans J. Crump-Weisner, U.S. Geological Survey, Water Resources Division, Washington, D.C. 20242

Data gathered from limited monitoring activities and project studies in several States indicate the ubiquitous occurrence and distribution of polychlorinated biphenyls in the aquatic environment. Residues have been detected in samples collected in several States, including Connecticut, New York, Pennsylvania, Virginia, South Carolina, Florida, Mississippi, Texas, Arkansas, and California. Data indicate concentrations ranging from 0.1 µg/l to 4 µg/l in unfiltered water samples and 0.5 µg/kg to 3200 µg/kg in bottom material. Some PCB residues were found in fish and aquatic plants. Samples were prepared by the same techniques used for general chlorinated insecticide detection, with special attention to clean-up and separation of PCB's from other compounds. Basic identification and quantification were made by dual-column electron-capture gas chromatography. Confirmation was accomplished by gas chromatography-mass spectrometry whenever possible. The sampling program is expected to be broadened geographically in 1973, and increased in successive years in order to more adequately assess the presence of PCB residues in major drainage basins of the contiguous United States, Hawaii, and Puerto Rico.

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WATER

17. COMPOSITIONAL CHANGES OF CHLOROBIPHENYL MIXTURES IN ANAEROBIC LAKE SEDIMENTS. Richard D. Vietzke and Gilman D. Veith, Water Chemistry Program, University of Wisconsin, Madison, Wisconsin 53706.

The compositional changes of chlorobiphenyl mixtures in anaerobic sediments have been investigated by incubating Aroclor 1254 in littoral sediments from Lake Michigan - Green Bay. Replicate samples of 25 ml wet sediment (10 gm dry weight) containing 100 ug of Aroclor 1254 were sealed and incubated at 30° C. Duplicate samples were analyzed periodically. The analysis of chlorobiphenyls in sediments has been evaluated using exhaustive solvent extraction and steam distillation methods. Because steam distillation removes chlorobiphenyls from sediments more rapidly than does solvent extraction and eliminates the need for liquid chromatographic cleanup procedures, a modified Dean - Stark apparatus has been developed for the sediment analysis. Refluxing acidified sediments for four hours results in the transfer of approximately 85 percent of Aroclor 1254 from the sediments to the cold hexane trap. The extract is dried with anhydrous Na_2SO_4, refluxed over clean, powdered copper to remove elemental sulfur, and analyzed by electron capture gas chromatography. This paper will discuss the changes in the chlorobiphenyl concentrations during the four-month incubation period.

18. POLYCHLORINATED BIPHENYL LEVELS IN HUMANS. A. R. Yobs, State Services Branch, Div. of Pesticide Community Studies, Off. of Pesticides Programs, EPA, Chamblee, Ga. 30341.

Polychlorinated biphenyls (PCBs) have been reported in many different parts of the environment. Previous reports of PCBs in humans have been few in number and have generally been concerned primarily with analytical procedures, reporting findings in only a few individuals. This report presents results from a human monitoring program in which samples have been routinely analyzed for these materials since April 1971. Case reports are presented in selected instances.

TUESDAY AFTERNOON - SYMPOSIUM ON PCB'S - STILL PREVALENT - STILL PERSISTENT - (Continued) - Joint with Division of Pesticide Chemistry - C. G. Gustafson, Presiding

PCB'S II - ANALYSIS AND DEGRADATION

19. ANALYTICAL ASPECTS OF POLYCHLORINATED BIPHENYL DETERMINATIONS IN HUMAN AND ANIMAL ADIPOSE TISSUE. F. J. Biros, M. Y. Enos, A. C. Walker, and J. F. Thompson, EPA, Perrine Primate Lab., P.O. Box 490, Perrine, Fla. 33157. A. R. Yobs, EPA, Div. of Pest., Community Studies, Offic. of Pesticides Programs, Chamblee, Ga. 30341.

An analytical evaluation and comparative study have been performed to establish and improve the efficacy of a method employed routinely for semi-quantitative determination of polychlorinated biphenyls (PCB) in tissue samples by thin layer chromatography (TLC). (Mulberg, B. et. al, Abstr. 84th ann. meeting, AOAC, Oct. 1970). Quantitative results obtained at various stages of the TLC procedures to eliminate interferences from organochlorine pesticide residues, have been compared with those obtained by total area measurements of gas-liquid chromatograms of the same tissue samples. These evaluations have resulted in modifications of the original procedure and recommendations concerning the choice of Aroclor standard used in the semi-quantitative estimation of sample PCB concentration. Additional studies have been performed to establish quantitative PCB levels in human and animal tissue samples which would (a) escape detection, and (b) be expected to lead to ambiguities in the estimation of levels of certain organochlorine pesticide residues including DDT and its isomers, analogs, and metabolites concurrent in the sample. A total of 140 general population adipose tissue samples have been subjected to analysis by combined gas chromatography-mass spectrometry to confirm and identify PCB components stored in human adipose tissue. Levels of total PCB ranged from 0.4 to 3.5 ppm. Representative chromatographic and mass spectral data will be presented in addition to identification of common PCB components encountered.

20. IDENTIFICATION OF PCB's IN THE PRESENCE OF DDT-TYPE COMPOUNDS USING LOW TEMPERATURE LUMINESCENCE. J. T. Brownrigg, J. Guilfoyle, and A. W. Hornig, Baird-Atomic, Inc., 125 Middlesex Tpk., Bedford, Mass. 01730.

Polychlorinated biphenyls (PCB's) interfere with gas chromatographic analyses of DDT and related compounds, necessitating a simple independent method for PCB and

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DDT determination. The purpose of the present study was to determine the applicability of low temperature (77° K) luminescence methods to this problem. Basic studies included documentation of excitation/emission spectra of 6 pesticides (p,p'- and o,p'-DDE, DDD and DDT), 7 PCB isomers, and 5 PCB mixtures (Aroclors). Although phosphorescence spectra of the DDD and DDT compounds are very similar, possible differences in lifetime and polarization measurements may aid in differentiation. Emission from DDE is at least 100X less intense than that of DDD or DDT, and is therefore more difficult to determine with adequate sensitivity. Spectral differences among various Aroclors are sufficient to allow those studied to be differentiated. In our work, emission from solvent impurities limited detection sensitivities t about 1.0 ppm for DDT/DDD and about 0.01 ppm for Aroclors. By removing interference, detection sensitivities should be improved by two orders of magnitude. Low temperature luminescence studies in various binary mixtures of Aroclor 1254 and p,p'-DDT indicate Aroclor 1254 may be identified and quantitated in the presence of DDT concentrations 100X greater. (Work supported by EPA Contract No. 68-01-0082)

21. QUANTITATIVE PCB STANDARDS FOR ELECTRON CAPTURE GAS CHROMATOGRAPHY. Ronald G. Webb, Ann C. McCall, Southeast Water Laboratory, College Station Road, Athens, Georgia 30601.

Solutions of Aroclors 1221 through 1260 have been prepared in which the weight of PCB present in each GC peak is known. These materials will be proposed as quantitative PCB standards. Their composition was determined by elemental analysis, gas chromatography with a Coulson conductivity detector, GC-MS, and EC in both the pulsed and D. C. modes. They can be used for PCB analysis of water, sediments, fish, and other environmental samples.

22. A COMPUTER ASSISTED GC-MS EXAMINATION OF FISH EXTRACTS FOR PCB AND PESTICIDE RESIDUES IN SILICIC ACID COLUMN FRACTIONS. David L. Stalling, Fish-Pesticide Research Laboratory, Route 1, Columbia, Missouri 65201.

Extracts of 20.0 g of fish from selected areas in the environment were prepared for mass spectrometry using a combination of gel permeation (GPC) and column adsorption chromatography. Extracts after GPC (using cyclohexane-Biobeads S-X2) were separated into 6 and 15% diethyl ether-pet ether fractions using Florisil®. The 6% fraction was resolved by GLC and concentrated prior to GC-MS examination. Reverse-phase TLC was also employed to examine the PCB fraction. The GC-MS computer system was a PDP-12 LDP computer interfaced to a Perkin Elmer 270-B GC-mass spectrometer. The MASH (Mass Spectrometer Handler) software system was used for data acquisition and preparation of mass fragmentograms. Spectra were acquired every 6-8 seconds for up to 33 minutes (up to 250 scans). A mass range of 14-555 was scanned and each spectrum was stored on magnetic tape. Mass searches for up to five combined masses were made on each set of spectra. The distribution and imidence of parent ions of the PCB homologues were indicative of PCB residues and mass fragmentograms greatly facilitate location of spectra for confirmation. Mixtures of PCB formulations as residues in fish are clearly indicated. The occurrence of Halowaxes® or chlorinated terphenyls have not yet been detected. The GC-MS computer system is one of the few available techniques for identification of these contaminants.

23. PHOTOCHEMICAL DEGRADATION OF ISOMERICALLY PURE DI-, TETRA-, HEXA-, OCTA- AND DECACHLOROBIPHENYLS. O. Hutzinger, W. D. Jamieson, S. Safe, National Research Council of Canada, Atlantic Regional Laboratory, Halifax, N. S., and V. Zitko, Environment Canada, Fisheries Service Biological Station, St. Andrew's, N. B., CANADA.

The photoinitiated degradation of 4,4-di-, 2,2',5,5'-tetra-, 3,3',4,4'-tetra-, 2,2',4,4',5,5'-hexa-, 2,2',3,3',4,4',5,5'-octa- and decachlorobiphenyls was investigated under natural and simulated natural (avoiding organic solvents, wavelength of irradiation >300 nm) conditions. In most experiments, thin films of sample were photolyzed in the presence of N_2O. From the abovementioned chlorobiphenyls, major products were those resulting from dechlorination and/or polymerization as well as polar compounds which had retained little or no chlorine. Qualitative analyses

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of products were by usual techniques such as GLC-mass spectrometry as well as by high resolution mass spectrometry using photoplate detection. Structures of degradation products will be discussed as will be conditions for their formation.

24. DEGRADATION OF PCB'S AS STUDIED BY OXIDATIVE ELECTROCHEMISTRY. James D. Stuart, Richard R. Keenan, Robert J. Fenn, Department of Chemistry, and Robert G. Jensen, Walter J. Pudelkiewicz, Pesticide Research Laboratory, University of Connecticut, Storrs, Connecticut 06268.

Although very resistant to oxidation, PCB's are oxidized at very high anodic potentials in moderately-dried acetonitrile solvent. The anodic voltammetry at a glassy carbon and shiny platinum microelectrode of Aroclor samples yielded an irreversible peak in the region of +2.2 Volts vs. (aqueous) SCE. A series of pure 2,5-chloro-substituted biphenyls, with increasing numbers of chlorine atoms ranging from one to ten, was studied by fast sweep electrochemical techniques. Voltammetric data showed that their anodic pathways involved the irreversible removal of one or more electrons followed by rapid chemical reactions whose unstable products were, in turn, further oxidized. Macroscale electrolyses, keeping the anode at a constant potential with a carbon felt or platinum mesh electrode, were used to produce sufficient amounts of the oxidative products. Coulometry indicated a large irreproducible electron count. After the initial removal of electrons from the π-aromatic system, the intermediate and final products suggest pathways that involve (a) hydrolysis through hydroxy compounds that in turn suffer further oxidation, (b) solvolysis of the cationic species, (c) intra-molecular oxidative coupling, (d) inter-molecular dimerization. Most follow-up chemical reactions between the unstable cationic species with traces of water invariably present as impurities in the acetonitrile solvent or between other nucleophiles added to the solution will be discussed lending support to the anodic pathways suggested.

25. DETERMINATION OF PCB and PCT IN PAPERBOARD SAMPLES. C.M. Thomas and L.M. Reynolds, Ontario Research Foundation, Sheridan Park, Ontario, Canada.

PCBs are now recognized as possible contaminants in paperboards, particularly those containing recycled material. During the course of analysing paper and board samples for PCBs, analytical problems were encountered due to the presence of components with very long retention times under GLC conditions that were used for the PCB analyses. This paper will describe our methods for PCB analysis in pulp samples, how the contaminants other than PCB were identified as polychloroterphenyls (PCTs), methods of analysis for PCTs, and how PCTs are now routinely analysed in the presence of PCBs. The procedure involved soxhlet extraction of the paperboard sample with hexane, followed by cleanup and separation using Florisil column chromatography. PCTs are quantitated using electron capture (H^3) and/or (Ni^{63}) gas chromatography. Recovery data substantiating the reliability of the method will be presented. Some discussion will relate to methods of confirmation involving GC-MS and perchlorination.

WEDNESDAY MORNING - SECTION A - SYMPOSIUM ON PCB'S - STILL PREVALENT - STILL PERSISTENT - (Continued) - Joint with Division of Pesticide Chemistry - J. I. Teasley, Presiding

PCB'S III - TOXICOLOGY AND PHYSIOLOGICAL ACTIVITY

26. PCB'S IN LAYING HENS. Helene C. Cecil, Joel Bitman, George F. Fries, L. W. Smith, and R. J. Lillie. Animal Science Research Division, Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Maryland 20705.

Polychlorinated biphenyls (Aroclors 1221, 1232, 1242, 1248, 1254, 1268), a polychlorinated triphenyl (PCT-Aroclor 5442) and a polybrominated biphenyl (PBB) were administered to 12 groups of 35 laying white Leghorn chickens at a dietary level of 2 or 20 ppm. Egg production, eggshell characteristics, body weight, feed consumption, mortality, fertility, hatchability, and progeny performance were measured. The transfer of dietary PCB, PCT, and PBB into eggs and carcass tissue of hens was determined. Rates of depletion (decontamination) of PCB residues in tissues were studied following withdrawal of dietary PCB. The patterns and rates of PCB, PCT, and PBB excretion were followed in feces of hens fed these materials. In addition, the fate of these polyhalogenated bi- and triphenyl compounds was studied during processing and recycling to rats and cows.

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27. EVALUATION OF RESIDUES OF AROCHLOR 1254 IN POULTRY PRODUCTS - R. H. Tasks; B. H. Armbrecht, Bldg. 339-D, Agricultural Research Center, Beltsville, Md. 20705; and H. J. Paulin, Bionetics Research Laboratories, Inc., Falls Church, Va. 22046.

PCB residues occurring in tissues and eggs from White Leghorn chickens following feeding or Arochlor 1254 at graded dietary concentrations are reported.

Broiler Phase: Chicks were initiated on an 8-week feeding study employing diets containing Arochlor 1254 at graded concentrations up to 10 mg PCB/kg of feed. Tissue samples for PCB analysis were collected from birds sacrificed at termination of the feeding period (no withdrawal period) and tissue residue depletion was followed for 3 weeks following termination of the feeding period.

Layer Phase: Chicks (Group A) were initiated on diets containing graded concentrations of Arochlor 1254 and maintained until onset of egg production. A parallel group of birds (Group B) were maintained on control diet until onset of egg production at which time feeding of test diets was initiated. Eggs from both PCB analysis and hatchability determinations were collected periodically. PCB residues and egg hatchability for Groups A and B were compared.

28. TOXICODYNAMICS OF AROCLOR(R) 1254 IN THE MALE RAT. D.L. Grant, C.A. Moodie, and W.E.J. Phillips, Research Laboratories, Health Protection Branch, Department of National Health and Welfare, Ottawa, Canada.

Male Wistar rats, 30 days old, were placed on a ground cube diet containing one of four levels (0, 2, 20 or 100 ppm) of Aroclor(R) 1254, a polychlorinated biphenyl (PCB), for 8 months and then on the basal diet containing no PCB's for a further 6 months. Five rats were killed from each group after 2, 4, 6 and 8 months to study accumulation of residues as well as biochemical, physiological and pathological changes. Rats were also killed at 10, 12 and 14 months to determine the reversibility of the changes. The blood, brain, heart, liver and fat were analysed for residues of PCB's and were found to be dose related. Consistently, the 20 ppm diet significantly ($P < 0.05$) decreased the vitamin A stored in the liver and increased the hepatic analine hydroxylase activity. This microsomal ensyme activity was also significantly increased by the 2 ppm diet after 4 and 6 months. Liver weight was significantly increased by the 100 ppm diet after 2, 4, 6 and 8 months and by the 2 and 20 ppm diet after 2 months. Rats ingesting the 2 ppm diet for 2 and 4 months were significantly heavier, while rats receiving the 100 ppm diet were lighter. Results of the pathological examination of the liver and kidney, the rate of depletion of body burdens of the PCB and reversibility of the physiological and pathological changes will be presented.

29. INDUCTION OF RAT LIVER MONOOXYGENASE ACTIVITY BY SELECTED PCB ISOMERS. J. C. Street[1] R. D. Goer[2], F. H. Urry[1], P. A. Boland[2], and S. Z. Riaz[1]. [1]Department of Animal Science, Division of Biochemistry, Utah State University, Logan, Utah 84321. [2]Department of Chemistry, Montana State University, Bozeman, Montana 59715.

Previous study in this laboratory established the range of liver monooxygenase activity induced by the Aroclor(R) PCB products. Such enzyme induction was shown to be a direct function of the percentage chlorine in these products and was highly correlated with their mean partition coefficients (determined as R_m values in reversed phase TLC). We now report the enzyme induction obtained with a series of PCB isomers administered in the diet of female rats for 15 days. Liver enlargement was minimal (1X) with the 2,5,2',5'-tetrachlorobiphenyl, fed at either 50 or 100 ppm in the diet. Hepatomegaly gradually increased to a maximum of 14 and 20% (respectively for those dosages) through the series 2,4,6,2',4',6'-hexachloro-, 2,5,2',4',5'-pentachloro-, 3,5,3',5'-tetrachloro-, decachloro-, and 2,4,5,2',4',5'-hexachlorobiphenyl.

Monooxygenase activities measured in the 10,000 x g supernatant of liver homogenates using EPN, p-nitroanisole, and aniline as substrates followed the same progression as the liver enlargement. The 2,5,2',5'-isomer increased these activities slightly but only at the 100-ppm dietary level (120, 106, 118% of control for the three substrates, respectively) while the most active isomer, 2,4,5,2',4',5'-hexachlorobiphenyl, led to values of 413, 358, and 247% of control at the 50-ppm dietary level. These activities were found to be inconsistent with the R_m values of the compounds. Similar investigation with asymmetric PCB isomers (only one ring chlorinated) will be reported.

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30. ENZYMATIC CHANGES IN THE LIVER OF RATS FED CHLORINATED BIPHENYLS, TRIPHENYLS AND DDT. James R. Allen and Lois J. Abrahamson, Department of Pathology, University of Wisconsin, Madison, Wisconsin 53706.

Similar morphological and biochemical changes occurred in the liver of rats receiving chlorinated biphenyls, triphenyls and DDT in the diet with the major variation being in the time required for changes to develop. The most obvious gross alteration was hypertrophy of the liver which developed within the initial 24 hours and persisted throughout the 30 day examination period. This increase in size was attributed primarily to proliferation of the smooth endoplasmic reticulum (SER) and to the formation of numerous large cytoplasmic concentric membrane arrays (CMA) within the hepatic cells. Homogenates prepared from these livers had increased levels of protein and RNA and decreased concentrations of DNA. The microsomal fractions of the hepatocytes had a decided increase in N-demethylase and nitroreductase while esterase levels were not altered appreciably. There were reduced levels of glucose-6-phosphatase and aromatic hydroxylase when expressed as a ratio to microsomal protein. These enzymatic changes were obvious within the initial 24 hours reaching a maximum deviations from the controls during the first week and leveling off thereafter. Animals that survived for 4 months showed a reduction in rate of gain, decreased hepatic SER, reduced numbers of CMA and decreased enzyme activities of the liver.

31. PHOSPHOLIPID SELECTIVITY IN REVERSAL OF BEEF BRAIN (Na^++K^+)ATPase INHIBITION BY POLYCHLORINATED BIPHENYLS AND DDT. C. W. Sharp and W. E. Wilson, Anal. Sys. Chemistry Branch, NIEHS, P. O. Box 12233, Research Triangle Park, N. C. 27709.

Since membranal (Na^++K^+)ATPases may play several important physiological roles, we have tried to ascertain the mode of action of polychlorinated biphenyls (PCBs) and DDT as inhibitors of the brain microsomal enzyme. In addition to chlorinated hydrocarbons (CHs), we investigated enzyme responsiveness to oleate, dodecyl sulfate and deoxycholate (DOC). At inhibitory concentrations, the CHs and detergents form oil-in-water dispersions or micelles; thus, limiting conditions were determined for reversal of and protection against enzyme inhibition by the CHs and the detergents. (Na^++K^+)ATPase responsiveness to the detergents exhibits a thermal dependence which is not observed for CHs. Albumin or the phospholipids can protect against or reverse inhibition by oleate or dodecyl sulfate. (Na^++K^+)ATPase responsiveness to phosphatidyl serine (PS) and, to a lesser extent, to phosphatidyl inositol (PI) contrasts with that to phosphatidyl choline or to phosphatidyl ethanolamine in two respects: (1) PS and PI can reverse enzyme inhibition by DDT and by PCBs. (2) PS and PI can protect the enzyme from severe inhibition by DOC. PS and/or PI are also effective as activators of phospholipase-treated (K. Taniguchi and T. Tonomura, J. Biochem., 69, 543, 1971) or DOC-solubilized (K. P. Wheeler and R. Whittam, J. Physiol., 207, 303, 1970) preparations of brain (Na^++K^+)ATPase. Should each of the various observations of phospholipid selectivity have a common significance, it could be hypothesized that DDT and the PCBs may effect their inhibitory action by interfering with normal phospholipid stabilization of the brain (Na^++K^+)ATPase.

32. DYNAMICS AND METABOLISM OF POLYCHLORINATED BIPHENYLS (PCBs) IN COLD EXPOSED PIGEONS. A.S.W. deFreitas, R.J. Norstrom, National Research Council of Canada, Ottawa K1A 0R6; O. Hutzinger, NRCC, Halifax, Nova Scotia, Canada.

Metabolism of PCBs in cold exposed White Carneau pigeons occurred most rapidly immediately after dosing, slowing down to a much lower rate after storage of the PCBs was complete. The relative rate of this initial metabolism of the various component peaks appeared to be similar over a fifty fold range in total dose. Movement from adipose tissue to muscle, brain and liver tissues occurred during starvation-induced utilization of half their lipid reserves. On subsequent refeeding the PCB content of these tissues returned to normal values. Similar studies with DDT have shown the same effect. The enzyme systems involved in PCB metabolism are probably linked to glycolysis as a preferred energy source, since their metabolism was more pronounced during refeeding than during starvation-induced movement from adipose tissue. Essentially no metabolism of the hexachloro components was observed. However, preferential mobilization and/or metabolism of other Aroclor 1254 components suggested that the position of the chlorine atoms, as well as the degree of chlorination has an influence.

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WEDNESDAY MORNING - SECTION B - GENERAL - J. L. Monkman, Presiding

33. PARTICLE-BORNE STRONG ACID: OCCURRENCE, EFFECTS AND DETERMINATION (ETHIDE. Cyrill Brosset, Swedish Water & Air Research Laboratory, S-400 40 Gothenburg, Sweden.

Studies on the formation of strong acid on particles have shown that this process is dependent upon the time of suspension of a particle in different air spaces as well as of SO_2-concentration and humidity of these air spaces. Particle-borne strong acid, but also that formed as a result of the impact of SO_2 on different surfaces could be associated with two very severe effects: Firstly, the acidification of lakes and of the ground. Secondly, the harmful effect on human health arising when sulphuric acid is deposited in the lower respiratory tracts. As already pointed out by Larsen (AJPH, 1970), this could be interpreted as a synergistic effect of SO_2 and particles. It is therefore of importance that continuous measurements of strong acid in respirable dust are made in connection with close surveillance of mortality and morbidity as related to air pollution. Three major problems are associated with satisfactory measurement methods: 1) Adequate sampling 2) Suitable filters for collection of particles and 3) Determination of strong acid in the aerosol sample. We are approaching the solution to 1) and 2), whereas 3) can now be regarded as solved.

34. THE APPLICATION OF SCALE FACTORS TO EMISSION STANDARDS. Mr. Robert D. Coleman and Professor Arthur C. Stern, Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina, Chapel Hill, North Carolina, 27514.

A linear programming model which produces a rational basis for determining the rate of change of allowable emission with change of source size, capacity or throughput is derived. It is designed to minimize cost of control to achieve air quality standards subject to the constraints of available technology. It provides a viable alternative to standards based solely on available technology, such as process weight standards, which do not directly consider cost or air quality considerations.

35. A CASE STUDY IN THE DEVELOPMENT OF AIR QUALITY MANAGEMENT STANDARDS-HYDROGEN CHLORIDE. Dr. Giuseppe Pumarola and Professor Arthur C. Stern, Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina, Chapel Hill, North Carolina, 27514.

Historically, hydrogen chloride was one of the first industrial pollutants regulated. Development of air quality management standards for it presents an illuminating case study of the problem of the interpretations of data on air pollution effects and on control technology. Of particular current interest is the evaluation of sensory and reactivity data from diverse sources.

36. THE RELATION BETWEEN CONCENTRATIONS OF SULFATE AND AMMONIUM IN AIR SAMPLES. L. Dubois, L. Kagan, T. Taichman, and J. L. Monkman. Air Pollution Control Dir., Environmental Health Centre, Tunney's Pasture, Ottawa, Canada.

Sulphate, a ubiquitous contaminant in a suspended particulate matter, has received some attention on account of the relatively high concentration. There is also a suspicion that sulfates may be partly responsible for the irritating properties of smog. With the present availability of specific ion electrodes for the ammonium ion, it becomes possible to study the ammonium to sulfate relationship on a large number of samples. At the same time, it has become feasible to monitor the genesis of ammonium sulfate in polluted air. Analytical comparison has also been made with ammonium ion levels obtained using other methods.

37. THE PHOTO-OXIDATION OF ISOPRENE IN THE PRESENCE OF NITROGEN DIOXIDE, CARBON MONOXIDE AND WATER VAPOR, by Daniel Lillian and Mark Antell, Dept. of Environmental Sciences, College of Agriculture & Environmental Science, Rutgers, the State University, New Brunswick, N.J. 08903.

Isoprene is a biologically generated atmospheric constituent suggested by theory and some experimental observations of undergoing tropospheric photo-oxidation similar to smog forming olefins.

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As such, it may play an important role in the formation of naturally occurring organic aerosol and the behavior of other atmospheric trace constituents such as ozone, $NO_{(x)}$, and CO.

A study was undertaken in our laboratory of the effects of simulated solar irradiation on mixtures of isoprene, NO_2, ozone, and other selected atmospheric constituents. The results of this study will be presented.

Based on the kinetics data obtained during the controlled irradiation, possible mechanisms for the photo-oxidation of isoprene will be discussed.

38. AEROSOL FORMATION FROM THE PHOTO-OXIDATION OF NON-LEADED FUELS
Daniel Lillian and David Hansen, Dept. of Environmental Sciences, College of Agriculture & Environmental Science, Rutgers, the State University, New Brunswick, N.J. 08903.

A study to characterize the formation of light scattering aerosol and condensation of non-leaded highly aromatic fuels is now in progress.

Gaseous mixtures of nitrogen dioxide and fuel, or its individual constituents, are blended in 200 liter Teflon bags. The bags are placed in a controlled temperature chamber and irradiated by a 10kw linear xenon lamp with suitable filtering for tropospheric solar simulation.

Variables measured as a function of time during the two irradiations include: condensation, nuclei, ozone, light scattering aerosol, oxidants, NO_x, and hydrocarbons. The effect of aromatic fuel content on these variables will be presented and the mechanistic implications will be discussed.

WEDNESDAY AFTERNOON - SECTION A - SYMPOSIUM ON PCB'S - STILL PREVALENT - STILL PERSISTENT - (Concluded) - Joint with Division of Pesticide Chemistry - C. G. Gustafson, Presiding

PCB'S IV - TOXICOLOGY AND PHYSIOLOGICAL ACTIVITY

39. METABOLISM OF ISOMERICALLY PURE MONO, DI-, TETRA- AND HEXACHLORO-BIPHENYLS BY MAMMAL, BIRD AND FISH. O. Hutzinger, D. Nash, S. Safe, National Research Council of Canada, Atlantic Regional Laboratory, Halifax, N. S., A. S. W. DeFreitas, R. J. Norstrom, National Research Council of Canada, Division of Biology, Ottawa, D. J. Wildish and V. Zitko, Environment Canada, Fisheries Service Biological Station, St. Andrew's, N. B.CANADA.

Commercial polychlorobiphenyl preparations, because of their complex isomer composition are unsuitable for a study of the metabolic change of these important environmental pollutants. Several unlabelled, chemically defined chlorobiphenyls have been administered to rats (50 mg/kg for 3 days) and comparative data for pigeons and brook trout are being obtained for 4-chloro-, 4,4'-dichloro-, 2,2',5,5'-tetrachloro- and 2,2',4,4',5,5'-hexachlorobiphenyl. Excreta were hydrolyzed, to liberate phenolic compounds from the glucuronic and sulfate forms, and feces and urine from treated animals compared to controls by thin-layer and gas chromatography. Mass spectrometry established that the main metabolite, in most cases, is a hydroxychlorobiphenyl which is formed by hydroxylation without replacement (loss) of chlorine. In each instance, the majority of the administered chlorobiphenyl appears unchanged in the feces. Attempts at establishing the structures of the metabolites by synthesis and 220 MHz NMR will be discussed.

40. ELIMINATION PATTERN OF AROCLOR 1254 COMPONENTS IN THE BOBWHITE. George L. Hoxter, EPA, Pesticide Regulation Division, So. Agriculture Bldg., Rm 1150, 14th and Independence Ave., S. W., Washington, D. C. 20250; Eugene Cromartie, Patuxent Wildlife Research Center, Laurel, Maryland 20810.

The elimination pattern of the components of Aroclor 1254 in the bobwhite quail(Colinus virginianus) was studies under laboratory conditions. Aroclor 1254 was administered

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as a dietary component at the rate of 300 ppm for a period of 14 days. Birds were then placed on untreated food and sacrificed at 14 or 42 days thereafter. At the end of test, three birds from the control group were each given an oral capsule dose of Aroclor 1254 in corn oil equivalent to 500 mg/kg body weight and were sacrificed after 1 hour. Analysis by combined gas chromatography - mass spectrometry was accomplished on several samples from each group of test birds. Chromatograms of the treated and untreated birds are presented. The chromatograms show that a dynamic system is at work, slowly removing certain components while increasing others. The GC profile for Arochlor 1254 did not maintain its integrity in bobwhite quail fed Aroclor 1254 for 14 days and clean food 14 or 42 days thereafter. Absorption of all components occurred at essentially the same rate, as shown by analysis of birds sacrificed an hour after a single oral dose of Aroclor. Significant alterations of certain PCB isomers appeared to take pla ?. Dechlorination was clearly apparent and isomeric transformation was suggested.

41. EFFECT OF DIETARY POLYCHLORINATED BIPHENYLS ON GROWTH AND REPRODUCTION OF MINK.
R. E. Bleavy, R. J. Aulerich and M. Ezbik, Departments of Poultry Science and Entomology, Michigan State University, East Lansing, Michigan 48823.

Reproductive failure or total early kit mortality has occurred in mink receiving diets that contain Lake Michigan coho salmon. Research indicates that an environmental pollutant of industrial origin such as the chlorinated hydrocarbons may be responsible. Feeding known dietary levels of DDT, its isomers and dieldrin far in excess of that found in coho salmon failed to duplicate the results. Adult mink were divided into three groups (12 females and 3 males) and fed either a basal ration, basal ration except for the substitution of 30% coho salmon for 30% organ fish, or the basal ration supplemented with 30 ppm PCB's (10 ppm each of Aroclors® 1242, 1248 and 1254). All mink receiving PCB's died within 121 days. Six mink fed the coho salmon died in this same period. Histopathological examination and PCB residue analysis were conducted. PCB content of brain, liver, kidney, spleen, lung, muscle and heart of mink that died when fed coho salmon or PCB supplementation was extremely similar. Brain content of PCB was about twice that of other tissues measured. Organ weights, expressed as percent of brain weight, were not significantly different. Feeding 10 ppm Aroclor 1254 significantly reduced body weight gains during the growing period. Combinations of Aroclor 1254 with either 0.3 ppm dieldrin or 10 ppm DDT further reduced body weight gains. Data on effect of continuous low-level feeding of Aroclor 1254 alone and in combination with DDT and/or dieldrin on mortality and reproduction will be presented.

42. TOXICITY AND PHYSIOLOGICAL ACTIVITY OF AROCLOR® 1254 TO SEVERAL ESTUARINE ORGANISMS,
D. R. Nimmo, D. J. Hansen, J. A. Couch, H.R.Cooley, and P. R. Parrish, Environmental Protection Agency, Gulf Breeze Laboratory, Sabine Island, Gulf Breeze, Florida 32561.

The polychlorinated biphenyl, Aroclor 1254, was detected in oysters from Escambia Bay Florida, for the first time in April 1969. The latest survey, 26 Oct. 1971, illustrates the extent of contamination: residues in biota ranged from non-detectable in plants to 10.0 parts per million (whole body) in fish (Menidia beryllina). Since 1969, much of our effort has been to study the effects of this chemical on species, populations, and ecosystems.

Population density of test tube cultures of the ciliate Tetrahymena pyriformis W at 96 hours was reduced significantly by 1.0 part per billion.

Chronic toxicities of Aroclor to seven species of estuarine organisms were determined in flowing-water bioassays. The minimum concentration that killed shrimp was 0.9 parts per billion. Fishes were killed and oyster growth was reduced at slightly higher concentrations. Residues in organs of shrimp (Penaeus duorarum) were greatest in the hepatopancreas, least in the abdominal muscle or exoskeleton. Grass shrimp (Palaemonetes pugio) accumulated Aroclor 1254 from water that contained concentrations less than 40 parts per trillion.

Tissue alterations were found in oysters, shrimp, and fish after chronic laboratory exposures to the chemical. Shrimp had the least detectable histological change--nuclear damage in hepatopancreatic cells. Oysters had more generalized tissue responses with heavy infiltration of leukocytes and atrophy of digestive diverticula. Fish had extreme vacuolization and necrosis of the liver.

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43. SOURCES, LEVELS, AND TOXICOLOGICAL SIGNIFICANCE OF PCB IN HATCHERY-REARED ATLANTIC SALMON. V. Zitko and O. Hutzinger, Biological Station, St. Andrews, N.B., Canada, and Atlantic Regional Laboratory, National Research Council of Canada, Halifax, N.S., Canada.

PCB residues found in hatchery-reared juvenile Atlantic salmon (1.2-3.7 μg/g wet weight, whole fish) originate from an antifouling paint, containing 6.5% of Aroclor® 1254. Fish food (PCB level 0.3-0.5 μg/g) is a minor source of PCB, leading to an equilibrium PCB level of 0.19 μg/g in fish never exposed to other PCB sources, and to a decrease from 1.97 to 0.78 μg/g in 120 days in fish removed from tanks painted with the antifouling paint. No buildup of PCB residues occurred in fish fed dry food containing 1.0 μg/g of Aroclor® 1254. An equilibrium level of 3.5 μg/g was reached in fish fed dry food with PCB level of 10.3 μg/g. Feeding food with PCB at 100 μg/g results in significant PCB accumulation (28 μg/g in 120 days). "Normal" mortality of fish could not be related to their PCB levels. A study of the toxicological significance of found PCB residues is under way. The PCB concentration in the antifouling paint decreases 50% on irradiation in air and changes only slightly on irradiation under water. Possible formation of chlorinated dibenzofurans under these conditions is investigated.

44. RESIDUE DYNAMICS AND BIOLOGICAL EFFECTS OF POLYCHLORINATED BIPHENYLS IN AQUATIC ORGANISMS. F. L. MAYER, Jr., P. H. Mehrle, Jr., H. O. Sanders. Fish-Pesticide Research Laboratory, Route 1, Columbia, Missouri 65201.

Toxicity residue dynamics and biological effects of polychlorinated biphenyls (PCBs) were investigated in several freshwater fishes and invertebrates. Acute toxicities (96-hr LC_{50}) of PCBs to fish ranged from 278 to 30,000 μg/l while those for aquatic invertebrates were 3.2 to 2,400 μg/l. The LC_{50} values for fish continuously exposed for 25 to 30 days varied from 3.4 to 433 μg/l and 5-to 10-day exposures of invertebrates resulted in LC_{50} values of 0.6 to 80 μg/l. Biological magnification of Aroclors 1248 and 1254 by bluegills was 26,300 to 71,400 times the levels in water after 60 days. Invertebrates exposed to Aroclor 1254 showed a residue magnification up to 47,000 times greater than in water. Dietary doses from 1.45 to 14,500 μg Aroclor 1254/kg body wt. per day to coho salmon had no effect on growth, nor produced observable toxicosis until death occurred in the highest dosage group after 260 days. Thyroid activity, as measured by 72-hr thyroidal ^{125}I uptake, was increased significantly. Stimulated thyroid activity occurred in salmon dosed with 1/1000th of that causing mortality. Dietary doses of Aroclors 1232, 1248, 1254, and 1260 to channel catfish at concentrations of 48 and 480 μg/g caused no mortality nor had any effect on growth. Thyroid activity was altered only by Aroclor 1254. The low dose increased thyroid activity by 56%, whereas a 91% increase was induced by the high dose. Implications concerning PCBs in the aquatic environment are discussed.

45. EXTENDING TOXICOLOGICAL INVESTIGATIONS. Joseph C. Street, Department of Animal Science, Division of Biochemistry, Utah State University, Logan, Utah 84321.

Discussion on the future of toxicological studies for the PCB's with both terrestrial and aquatic organisms.

46. PROSPECTS FOR THE FUTURE: FDA REGULATIONS AND TOLERANCE LIMITS. A. C. Colbye, Jr., U. S. Food and Drug Administration, Washington, D.C. 20000.

The Food and Drug Administration's regulations and tolerance limits for the PCB's will be discussed as well as the prospects regarding future PCB tolerance limits.

WEDNESDAY AFTERNOON - SECTION B - GENERAL - J. L. Monkman, Presiding

47. THE ORGANIC CONTENT OF STANDARD REFERENCE SAMPLES OF ASBESTOS. A. Zdrojewski, J. Bilborn, L. Dubois, and J. L. Monkman. Air Pollution Control Dir., Environmental Health Centre, Tunney's Pasture, Ottawa, Canada.

Some studies on the total organic and polycyclic hydrocarbon content of asbestos have been made under conditions which could have led to significant losses. Indeed, in some of the methods used complete evaporation of the solvent was made after extraction of the organic compounds.

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