Photochemical Dechlorination of Highly Chlorinated PCBs

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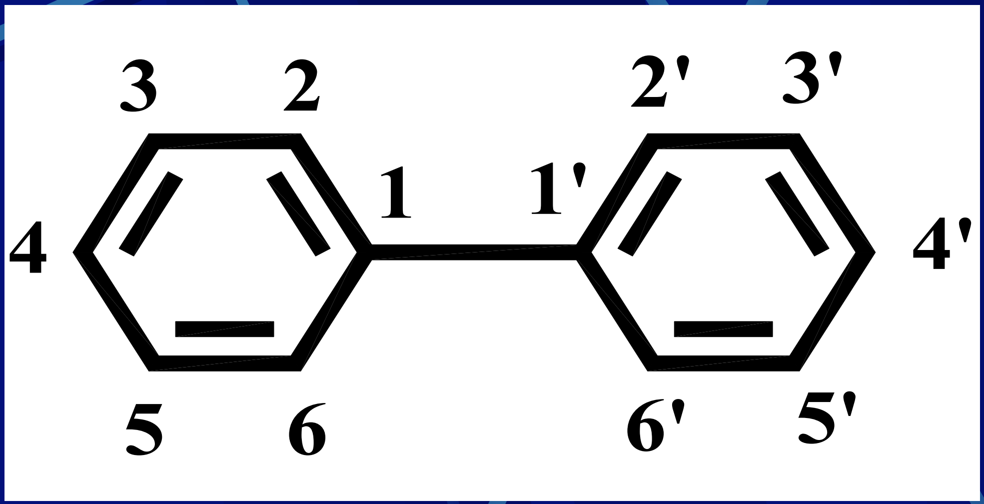
What are PCBs?

- Known as Polychlorinated Biphenyls
- Thermally stable organic compounds
- Used in transformer oils, high temp. lube oils, capacitors, fire retardants, inks and paints
- Commercially sold under brand names- Aroclor most common
- Loosely classified as highly and lower chlorinated PCBs

Generic PCB Structure



- $C_{12}H_{(10-n)}Cl_n$ (n=1 to 10)
- Chlorine atoms attached to different positions
- 206 different congeners
- Nomenclature: Aroclor 1254 contains 54% Cl

Concerns with PCBs

- Lipophilicity (or organophilicity)
  - Get adsorbed in soils and organic matter
  - Enter food chain through sediment dwelling microbes
  - Bioconcentration factor = 73,000
- Toxicity
  - Acute effects
    - facial edema, ocular discharge, swollen eyelids, conjunctival hyperemia, visual and hearing disturbances, low blood pressure, weakness and numbness of the extremities, neurobehavioural and psychomotor impairment, gastrointestinal upset, diarrhea, hepatitis, chloracne, and asymptomatic hyperthyroxinemia

Concerns with PCBs

- Non-carcinogenic chronic effects
  - damage to the liver, blood, immune system, nervous system and reproductive system
- Probable human carcinogens - USEPA

- Environmental Persistence
  - Known to exist “as is” for decades
  - Some anaerobic dechlorination may occur under favourable conditions
    - Requires soil microbe adaptation

Estimated Problem

- An estimated 1/3 of the US production (1.4×10^9 lbs) has been released into the environment – Weigel and Wu (2000)
- UNEP has identified PCBs as one of 12 Persistent Organic Pollutants (POPs) that need immediate attention

Remediation of PCB contaminated soils and sediments

Remediation Technologies

- Physical and Chemical Methods
  - Solidification and Stabilization
  - Vitrification
  - Soil washing
  - Proprietary processes (BEST, KPEG, KGME, CHLOROFF etc.)
- Thermal Desorption

Remediation Technologies

- Biological Methods
  - Aerobic microbes (*Burkholderia* sp. LB400) can degrade only lower chlorinated PCBs
  - Anaerobic Dechlorination feasible only on highly chlorinated PCBs
  - Issues
    - Requires anaerobic microbial adaptation
    - Slow growth of microbes
    - Temperature and nutrient requirements
    - Need to know when to switch from anaerobic to aerobic

Current Practice in Canada

- Incineration in special burners
- Incineration
  - Only two incinerators in Canada
  - Transportation and liabilities associated with it
  - Very expensive
  - Only known technology that is complete and known to work
- An area of intense research

Objective of the study

- Technology development for complete degradation of PCBs – A cradle to grave approach
- Would include
  - Extraction of PCBs from soils and sediments
  - Degradation of PCBs

Materials and Methods

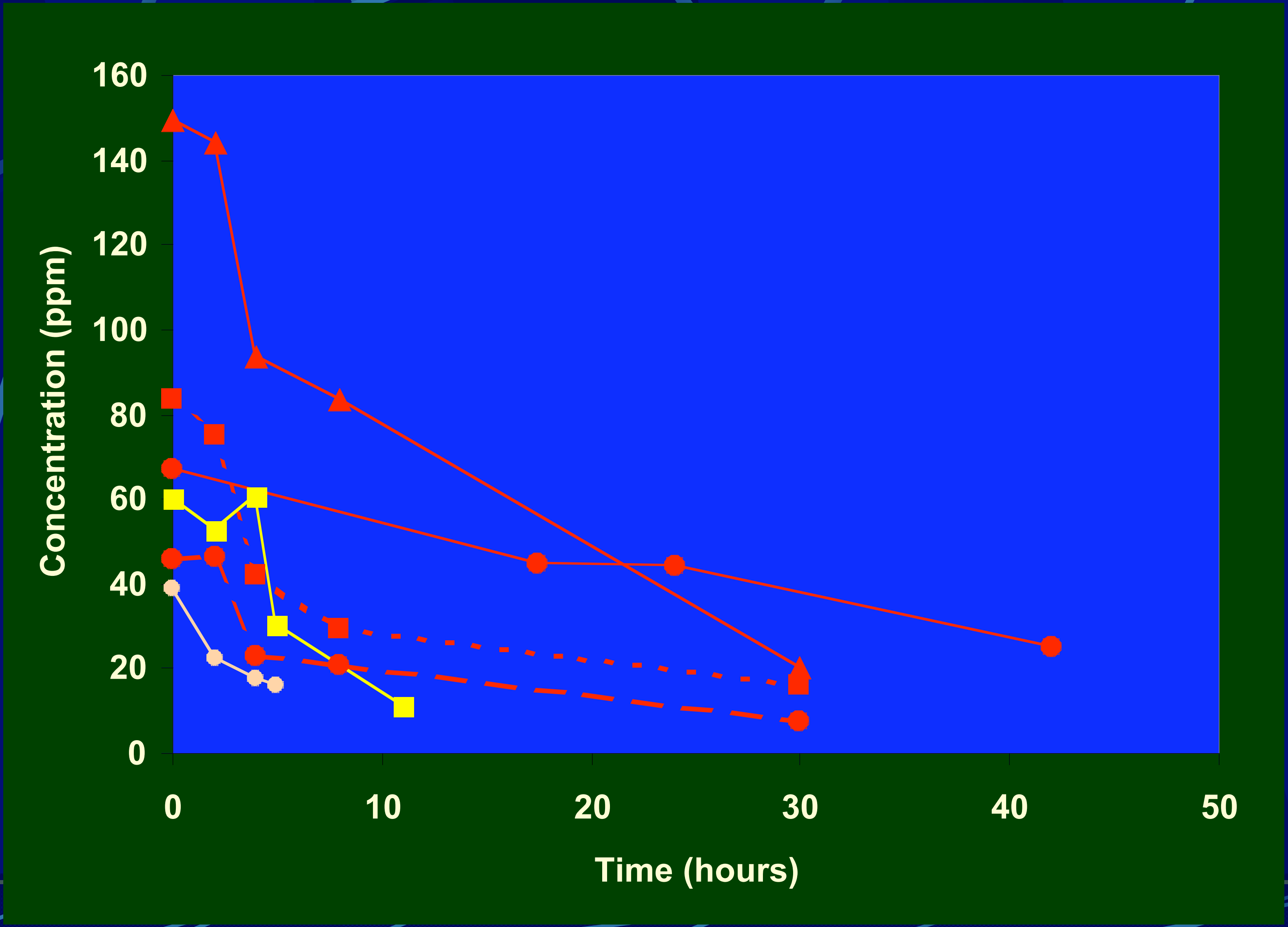
- PCB Type
  - Use commercial Aroclor 1254
  - Use extracted PCBs
- Photodegradation
  - Use ultraviolet (UV) light at 350 nm with phenothiazine (PT) as photosensitizer
  - Use commercial Aroclor 1254 pretreated with Fenton's reagent and then photodegraded using UV light at 350 nm with PT
  - Use UV light at 254 nm (without any catalyst or photosensitizer)

Results
Commercial Aroclor 1254

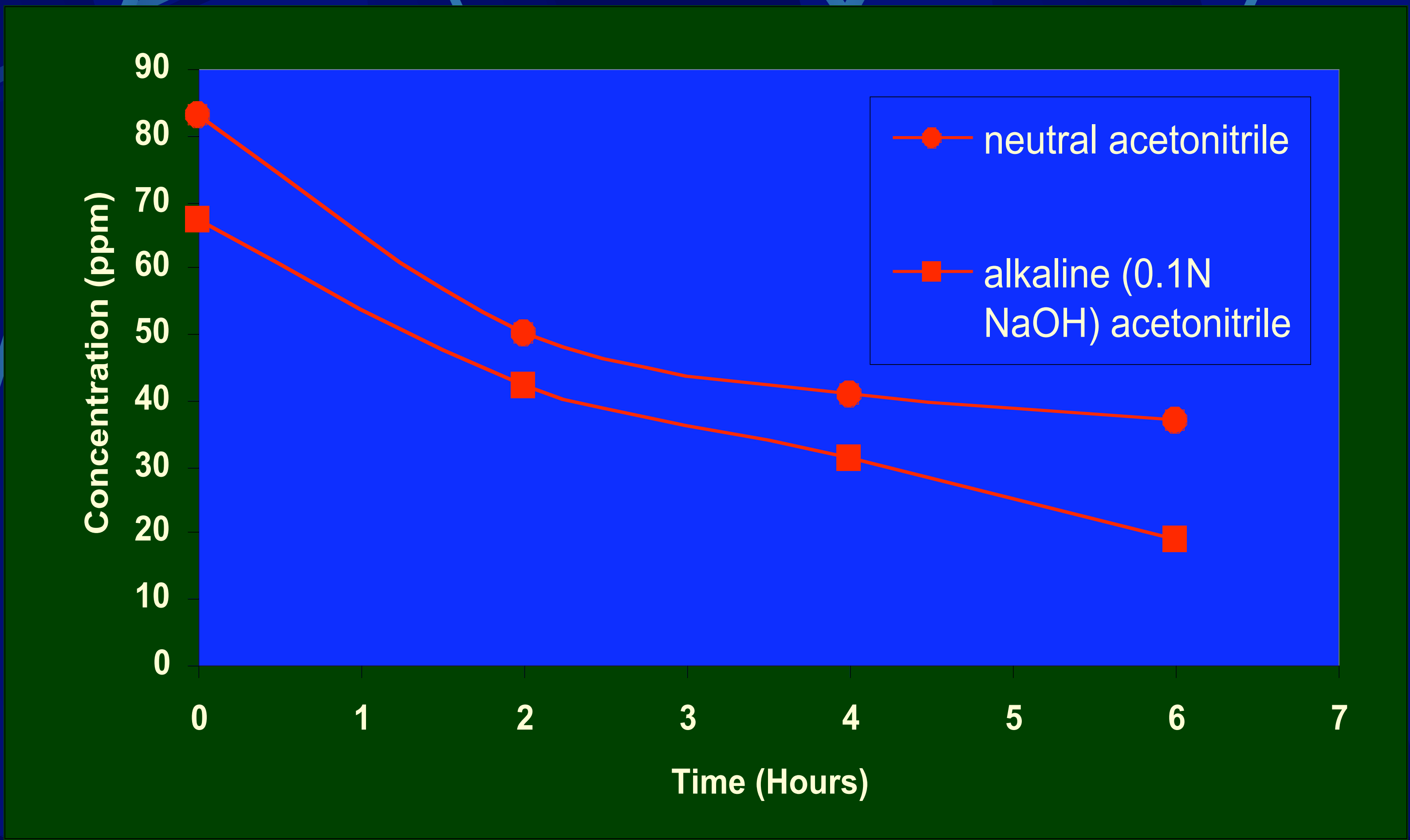
Results – PCBs subjected to 350 nm UV with PT as photosensitizer

- Intensity = 0.2 mW/cm^2
- Feasibility of Photodegradation
- Impact of Different Solvents
  - Hexane
  - Acetonitrile
  - Alkaline Isopropanol

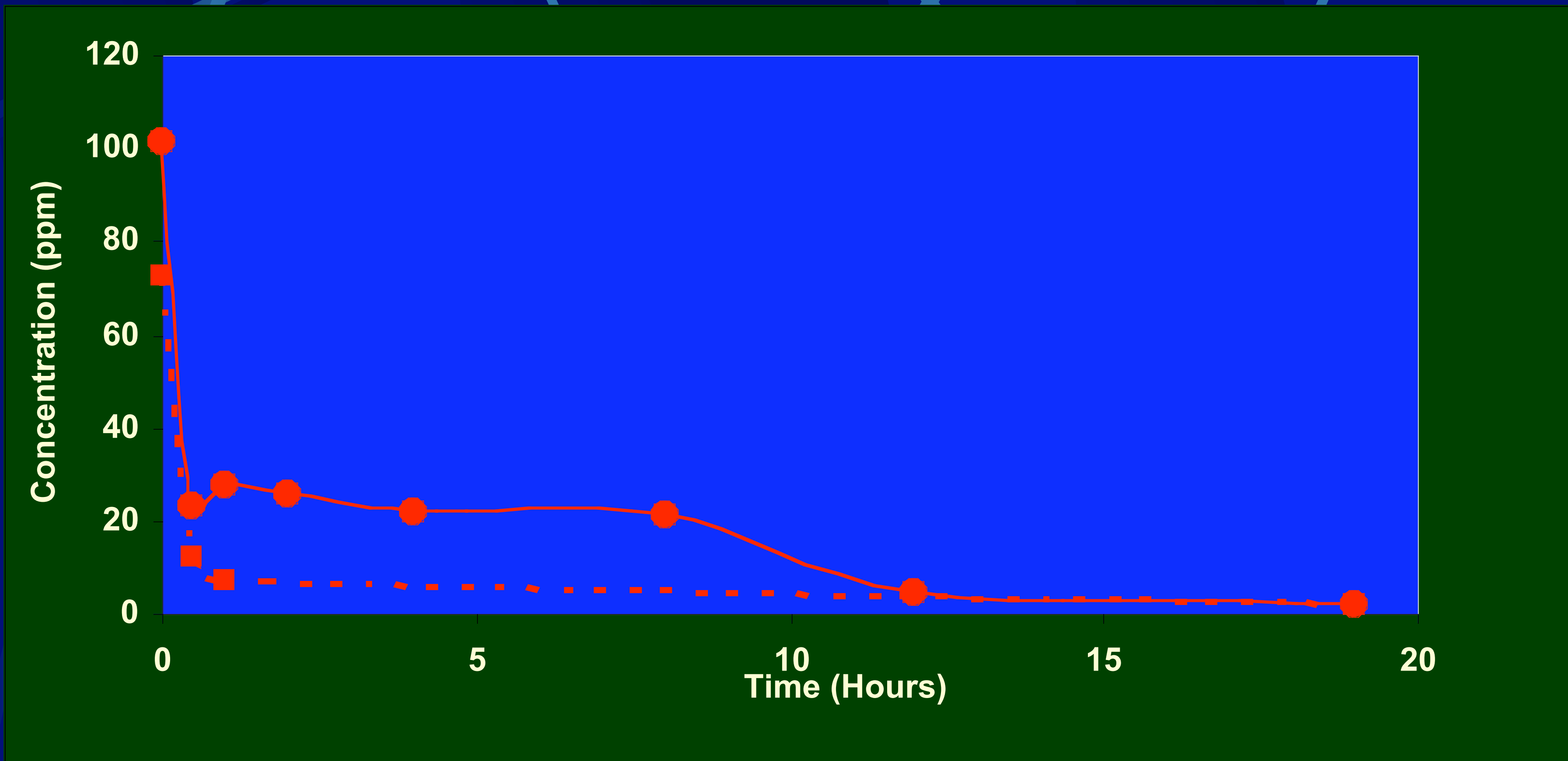
PCB Degradation in Hexane



PCB Degradation in Acetonitrile



PCB Degradation in Alkaline IPA



Change in chloride ion conc. with photodechlorination

Time (h)	0	0.5	1	2	4	6	8	19
Chloride ion conc. (mg/L)	0.0	1.11	1.48	1.35	2.12	2.02	2.52	4.03

Results – PhotoFenton Reactions

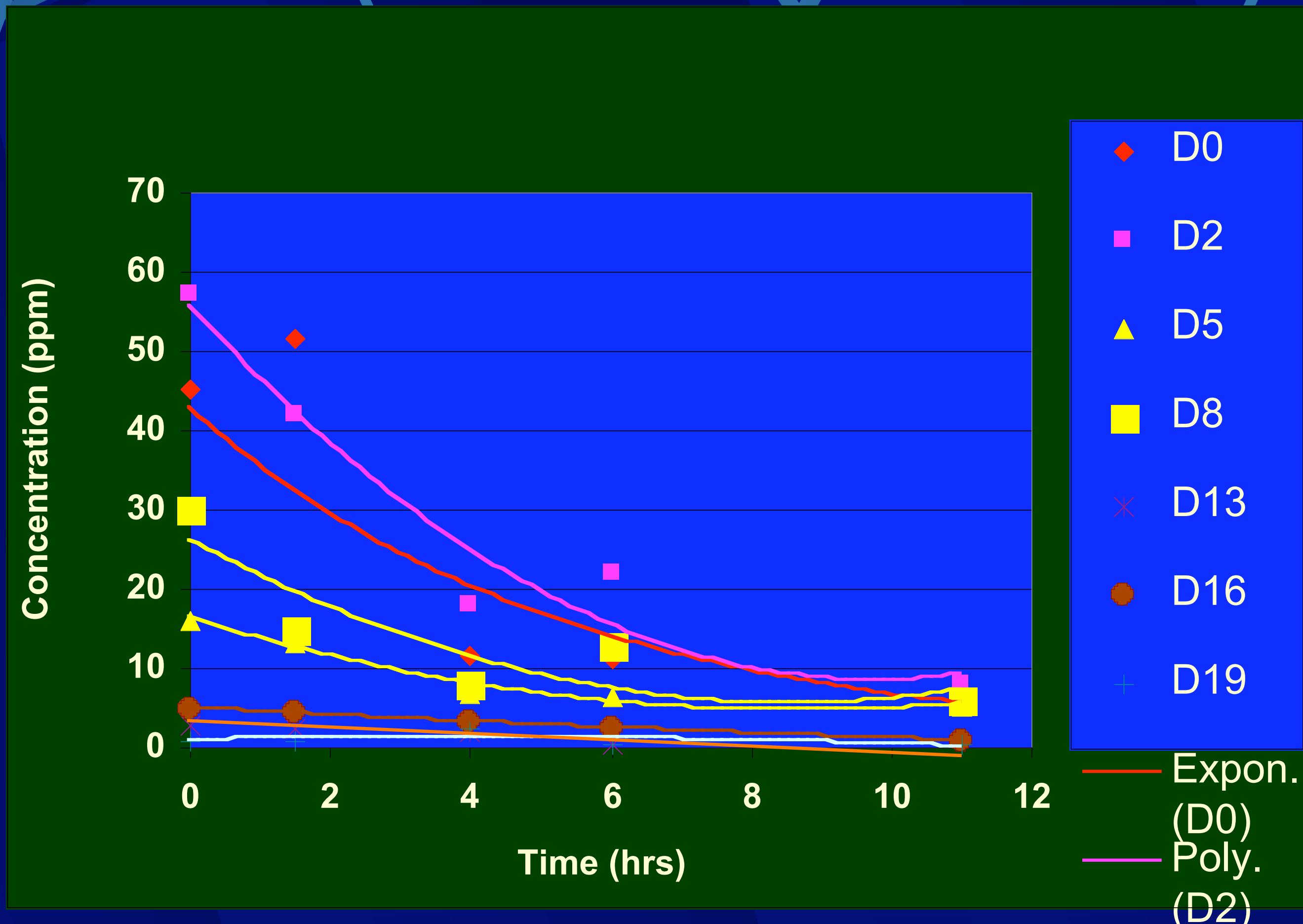
(Commercial Aroclor 1254)

- Impact of treating PCBs with Fenton's reagent followed by UV treatment (350 nm with phenothiazine)

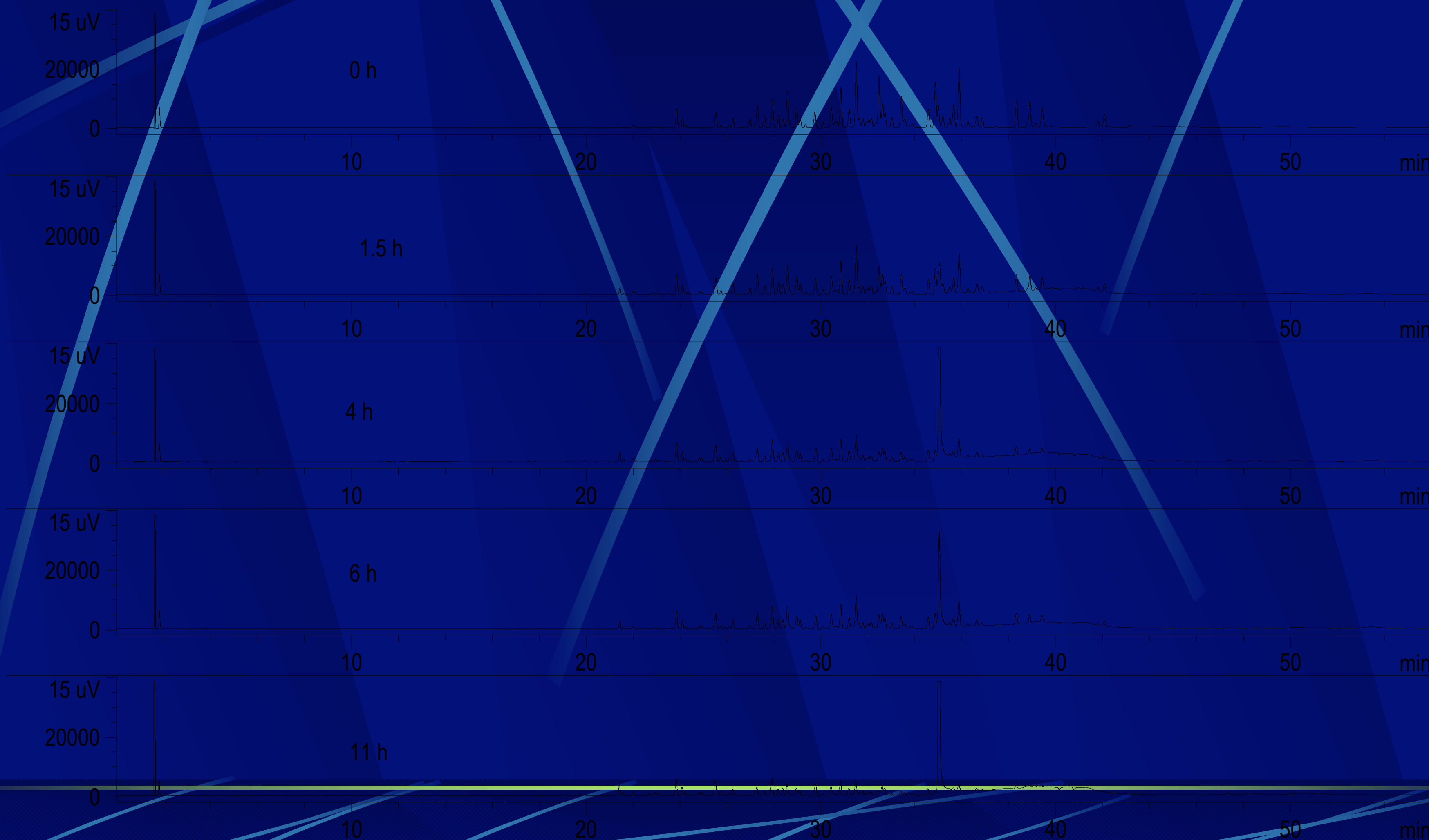
Fenton's Reactions

- $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH_–$
- $OH_– + C_xH_y \rightarrow H_2O + CO_2 + \text{heat}$
- $H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + HO_{2–}$
- $OH_– + Fe^{2+} \rightarrow OH^- + Fe^{3+}$
- $HO_{2–} + Fe^{3+} \rightarrow O_2 + H^+ + Fe^{2+}$
- $H_2O_2 + OH_– \rightarrow H_2O + HO_{2–}$

Photolysis of PCBs pretreated with Fenton's Reagent for varying periods using PT Sensitized UV light



Gas Chromatographs of PCBs pretreated with Fenton's Reagent followed by photodechlorination

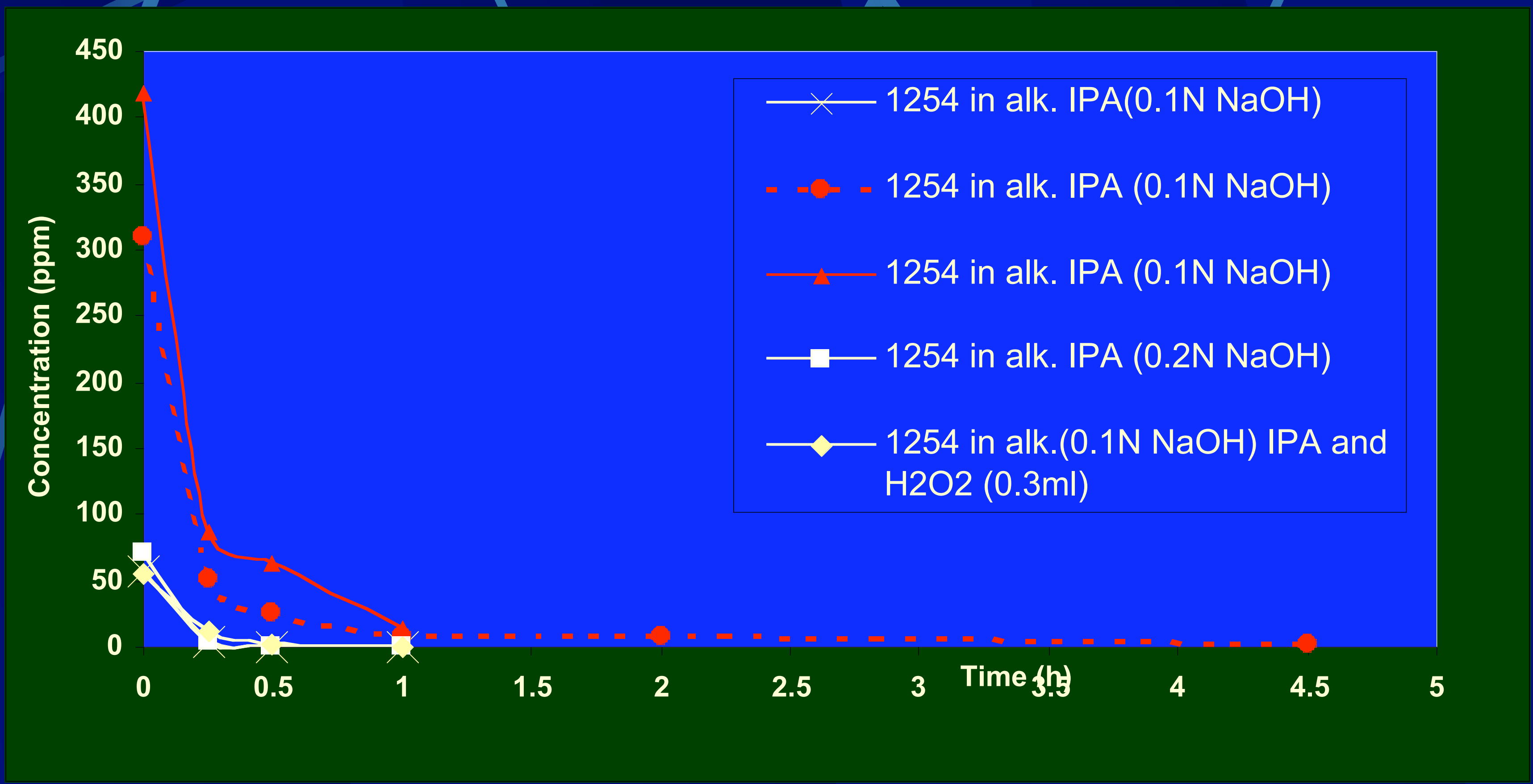


Results
Photodegradation (UV 254 nm) of PCBs in IPA

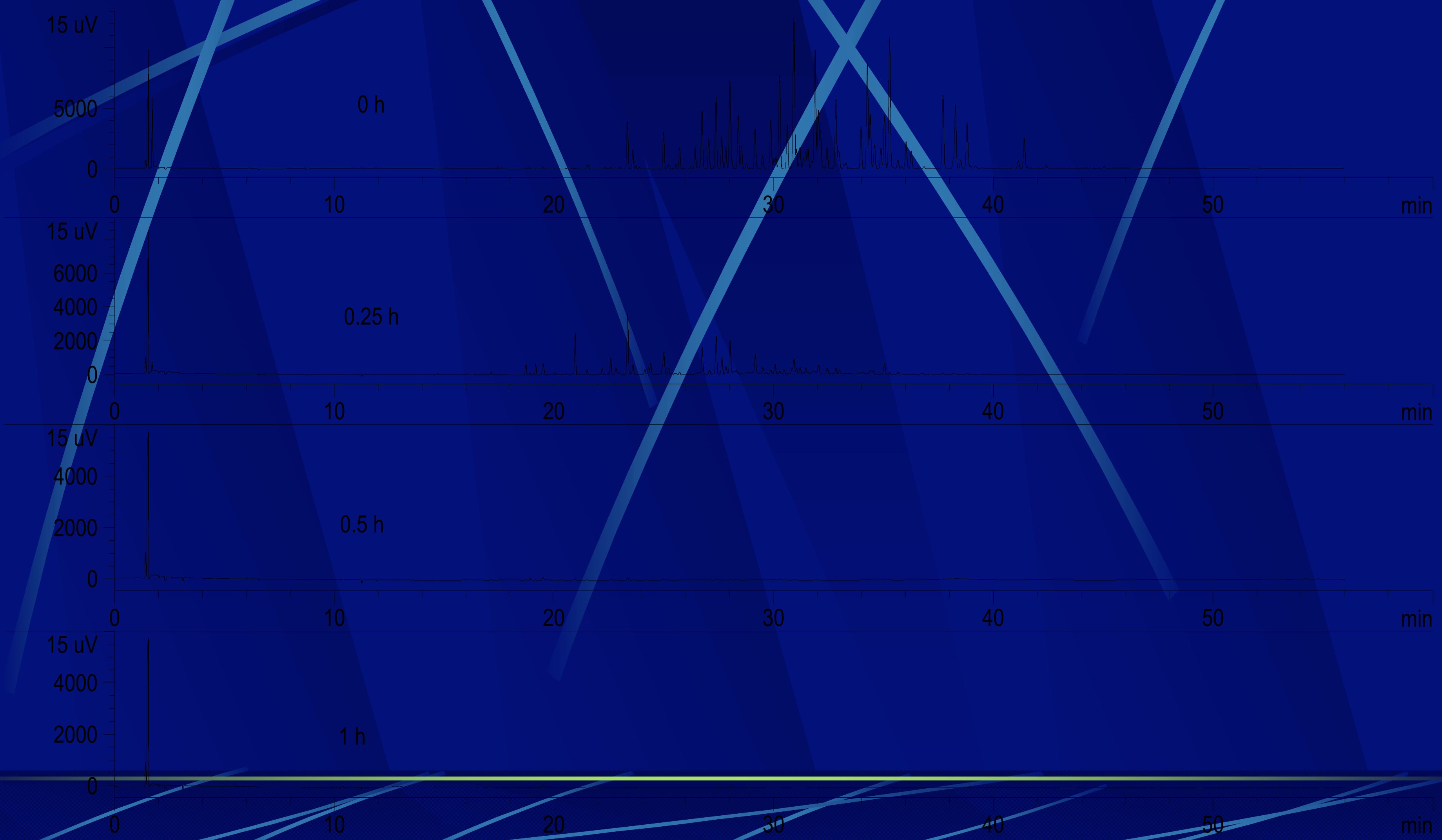
(Commercial Aroclor 1254)

- Intensity = 1.5 mW/cm^2
- Impact of varying alkalinity
- Impact of hydrogen peroxide addition
- Biphenyl production and degradation

PCBs degradation in UV 254 nm – impact of varying alkalinity and hydrogen peroxide

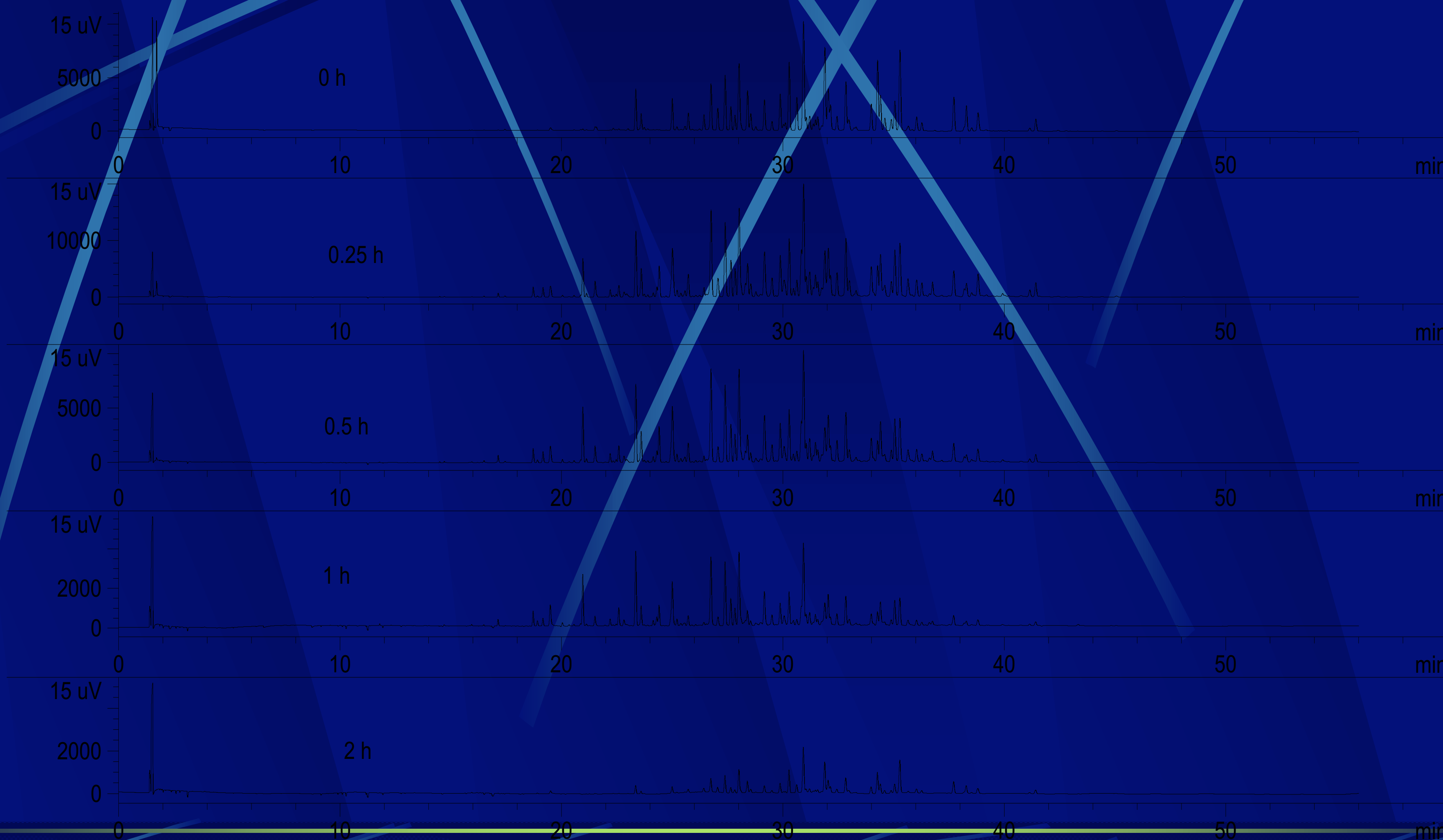


Dechlorination of 100ppm commercial Aroclor 1254 with UV (254nm) in alkaline (0.1N NaOH) IPA

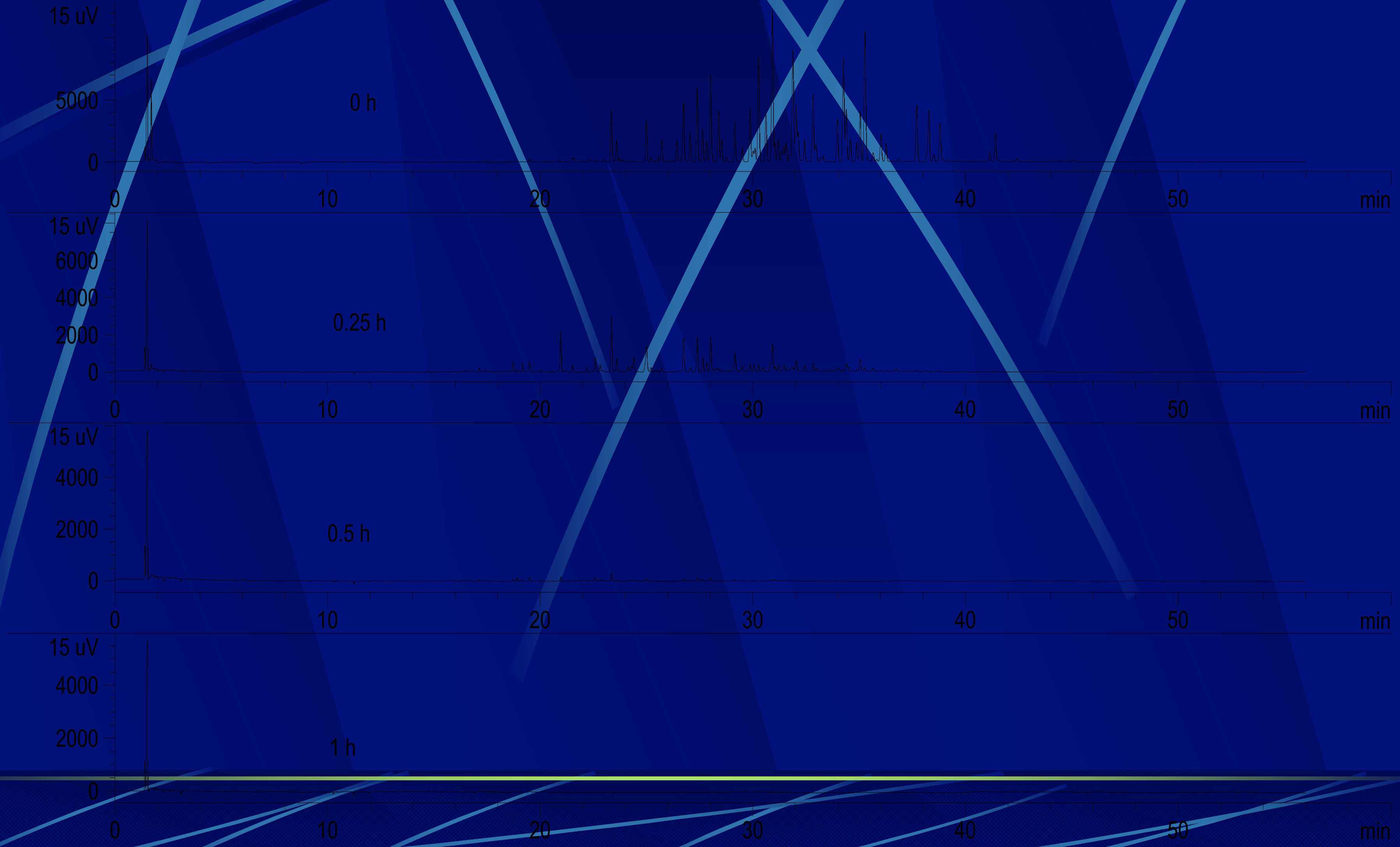


Dechlorination of 300ppm commercial Aroclor 1254 with UV (254nm) in alkaline (0.1N NaOH) IPA

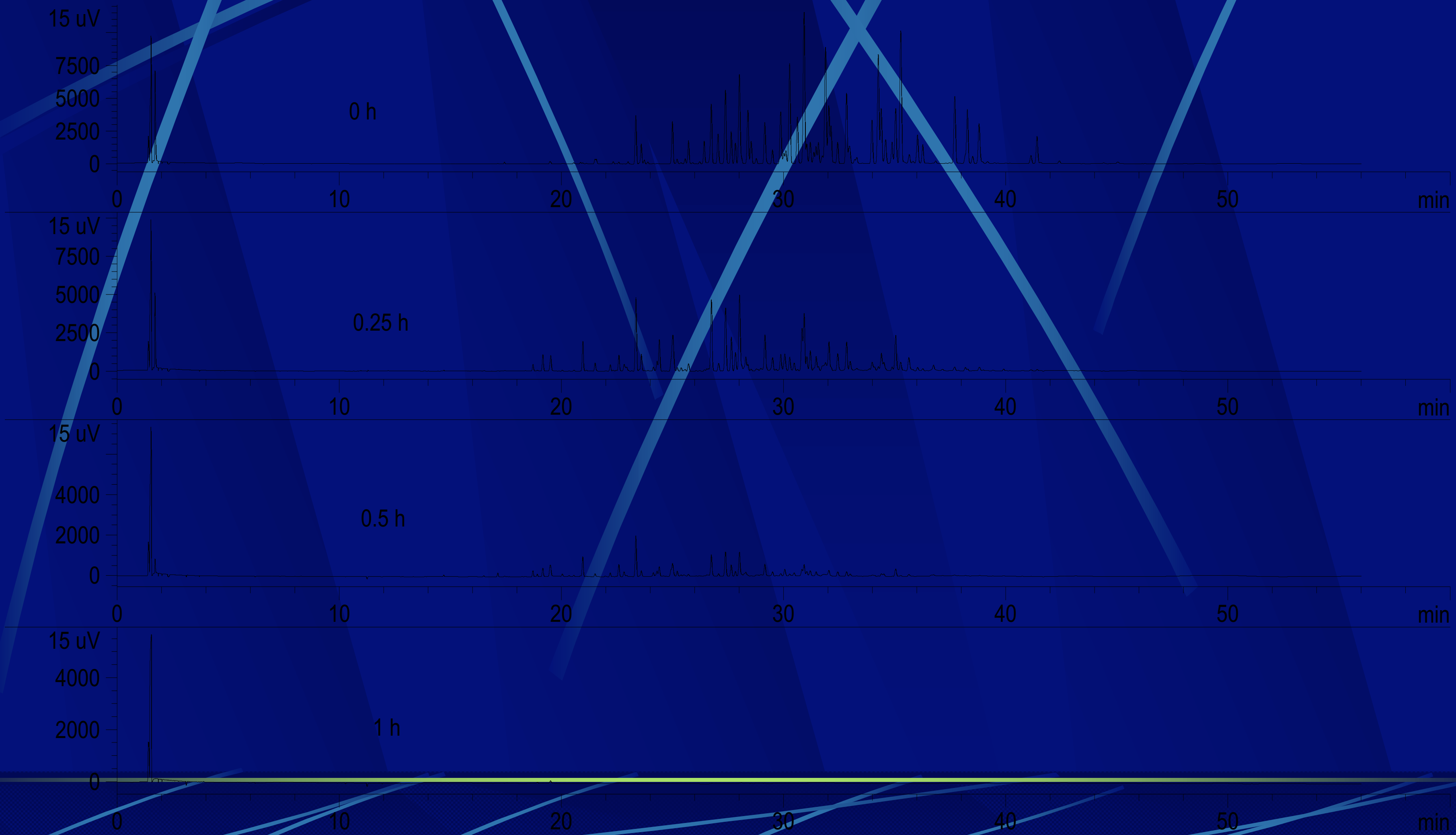
Dechlorination of 500ppm commercial Aroclor 1254 with UV (254nm) in alkaline (0.1N NaOH) IPA



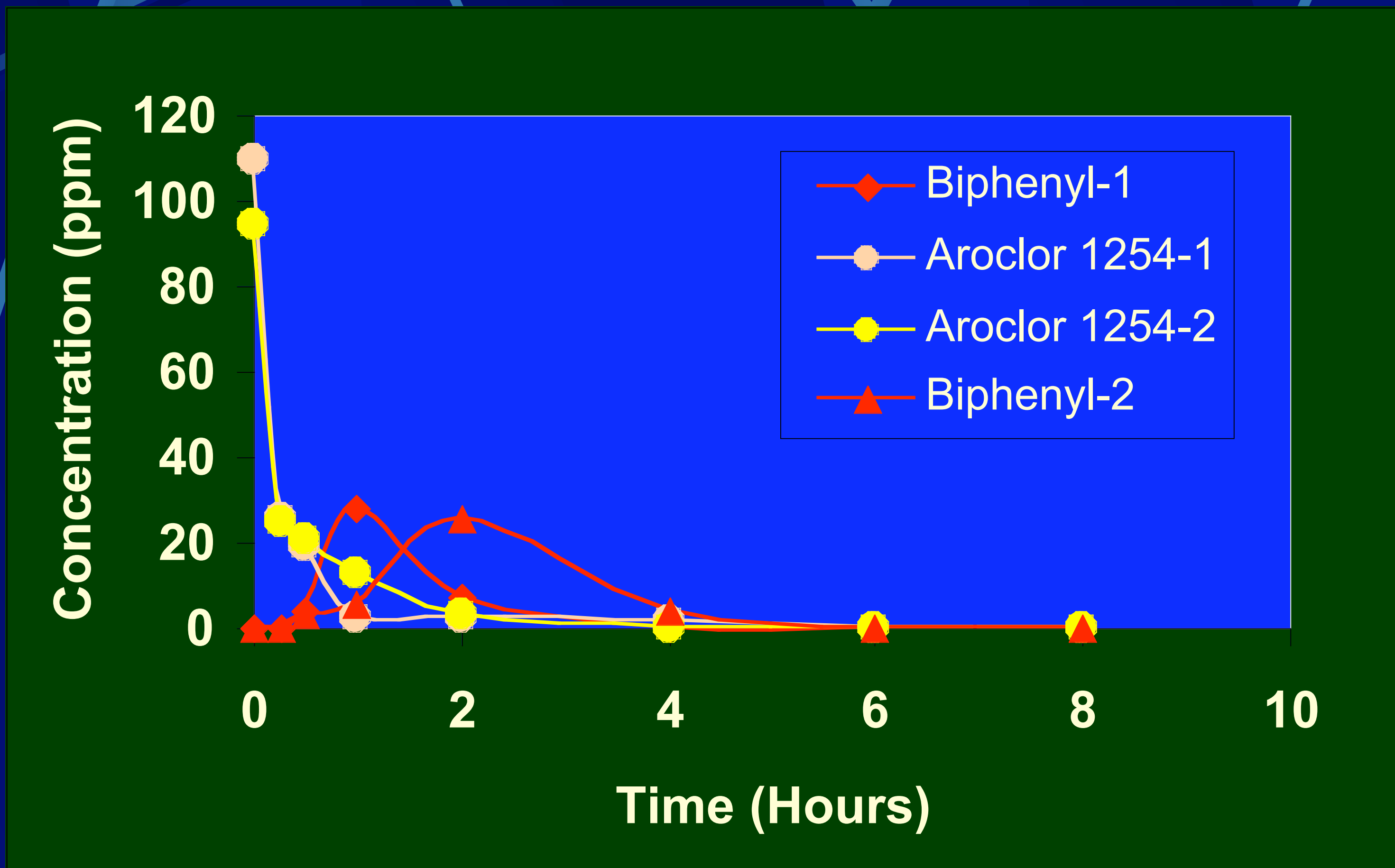
Dechlorination of commercial Aroclor 1254 with UV (254nm) in alkaline (0.2N NaOH) IPA



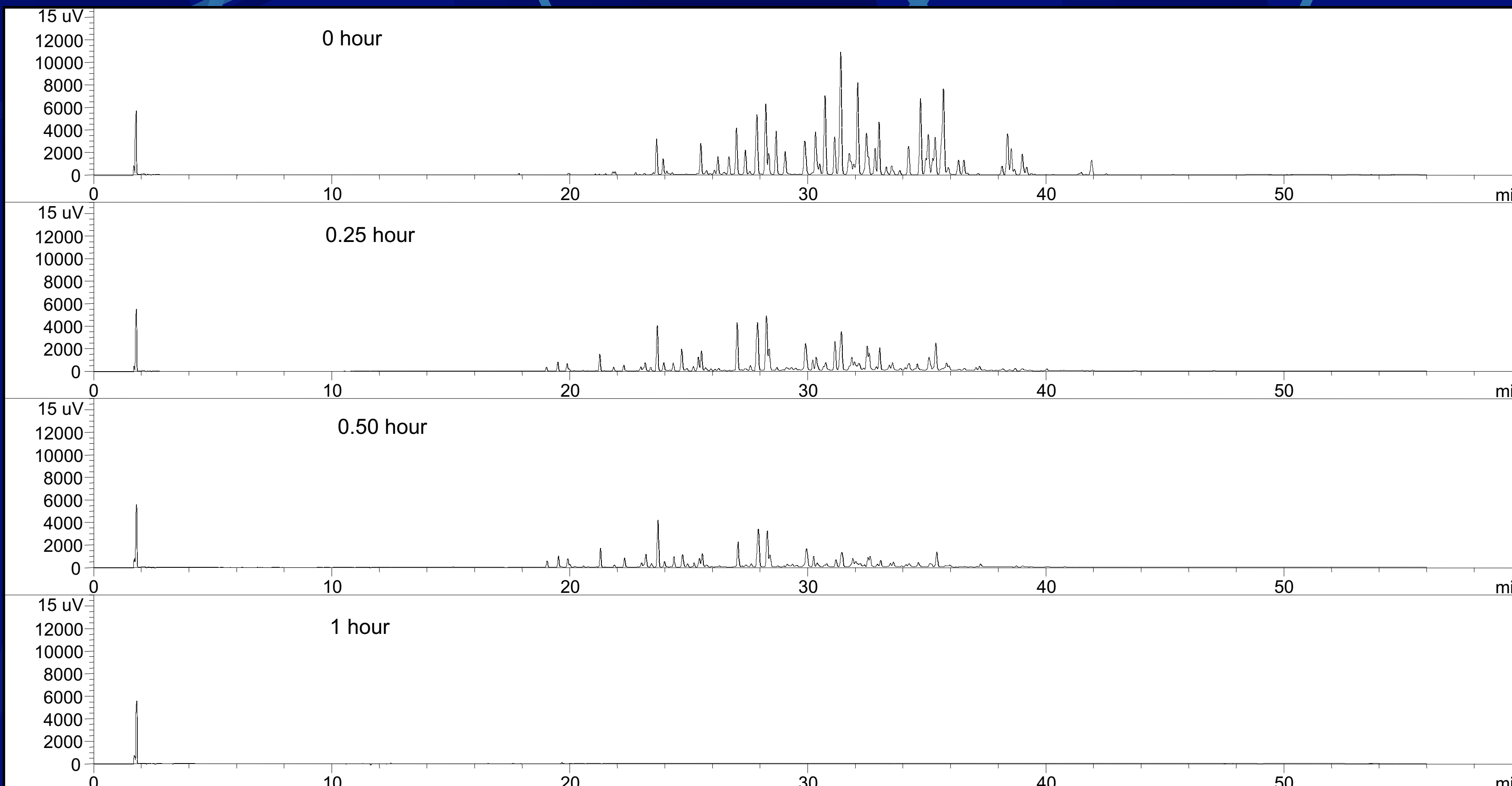
Dechlorination of commercial Aroclor 1254 with UV (254nm) in alkaline (0.1N NaOH) IPA and 0.5mL of 30%H_20_2



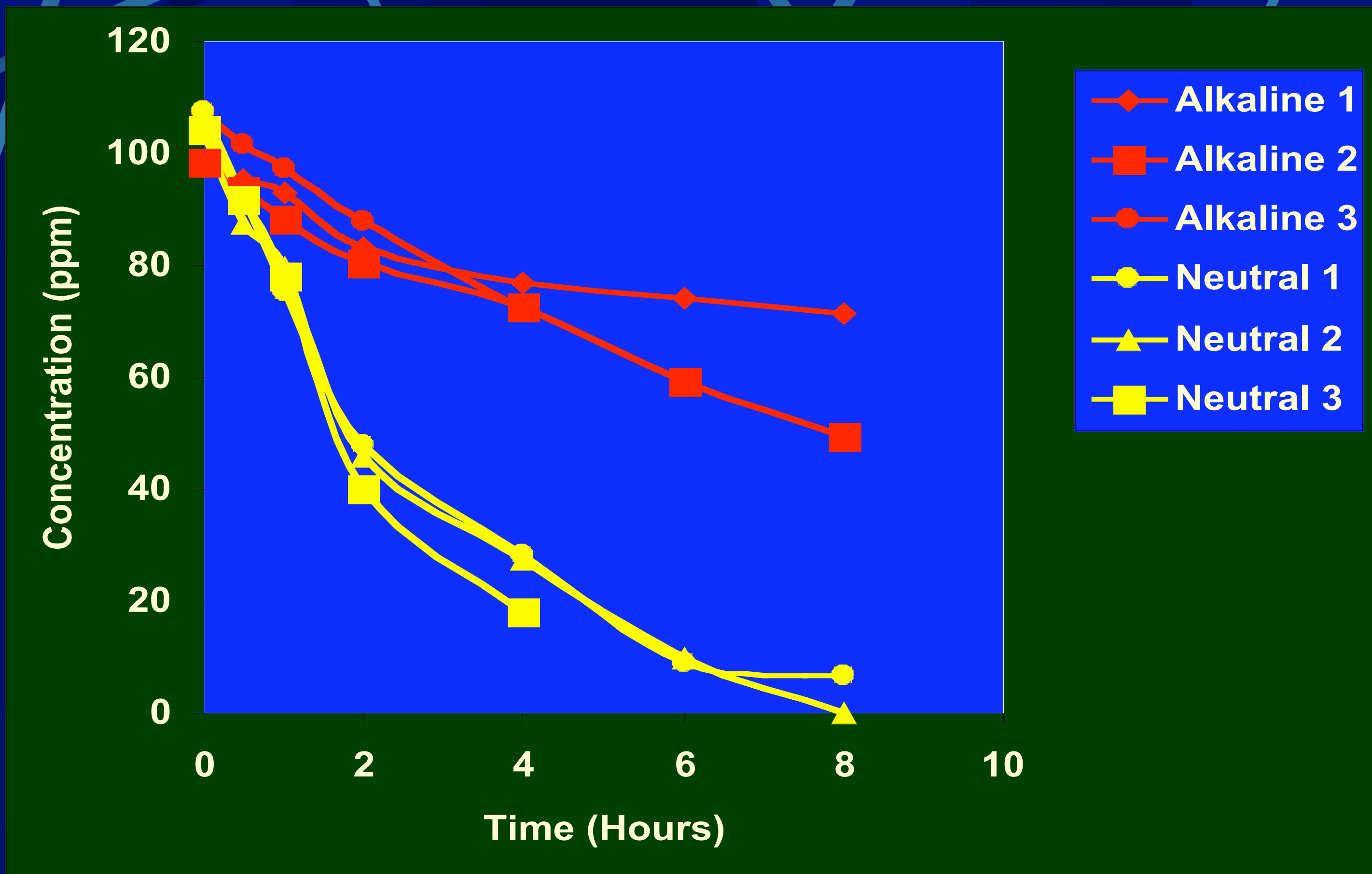
PCBs degradation in 254 nm UV – Biphenyl production and degradation



PCBs degradation in 254 nm UV – Biphenyl production and degradation

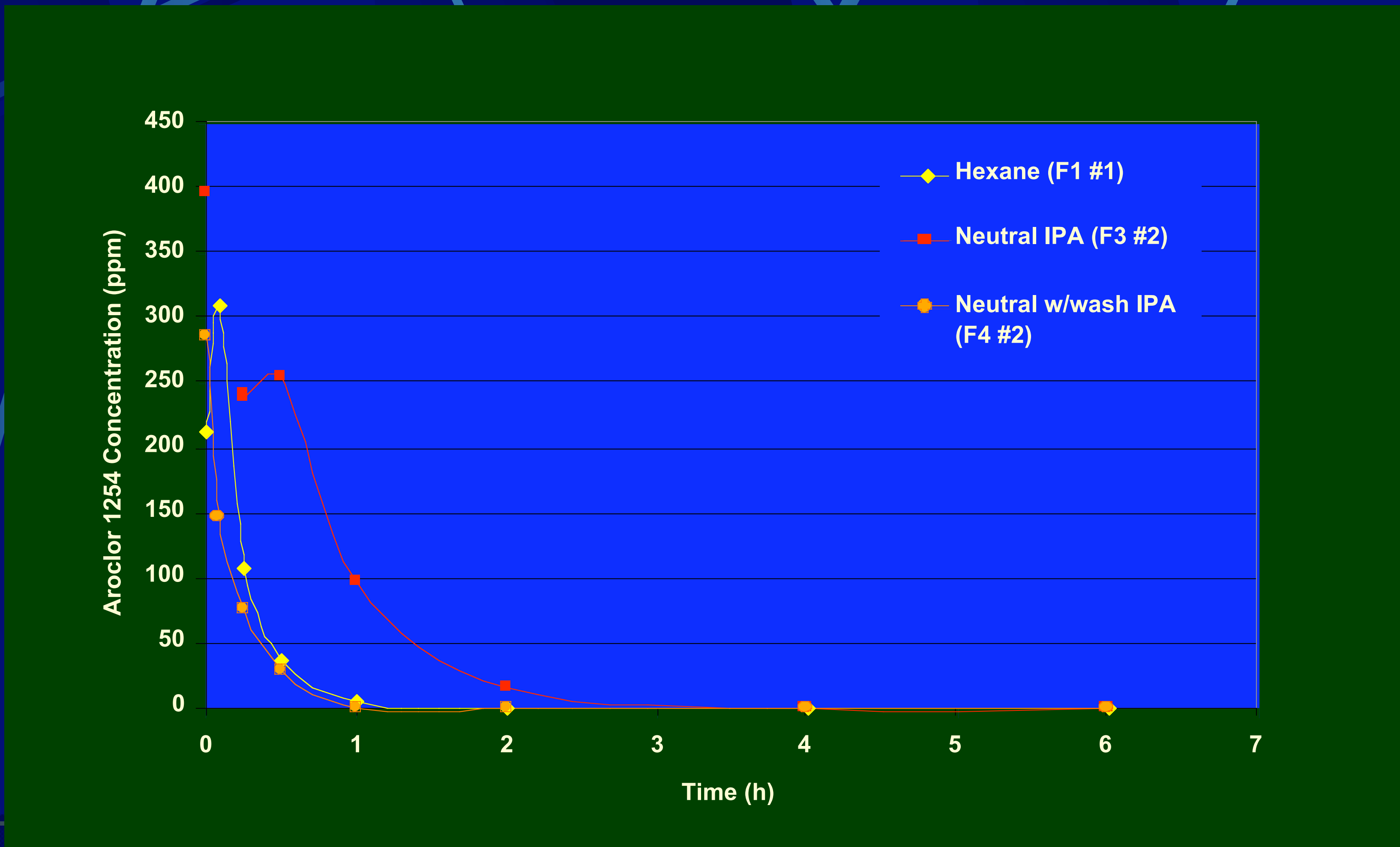


Biphenyl degradation with time (UV at 254 nm)

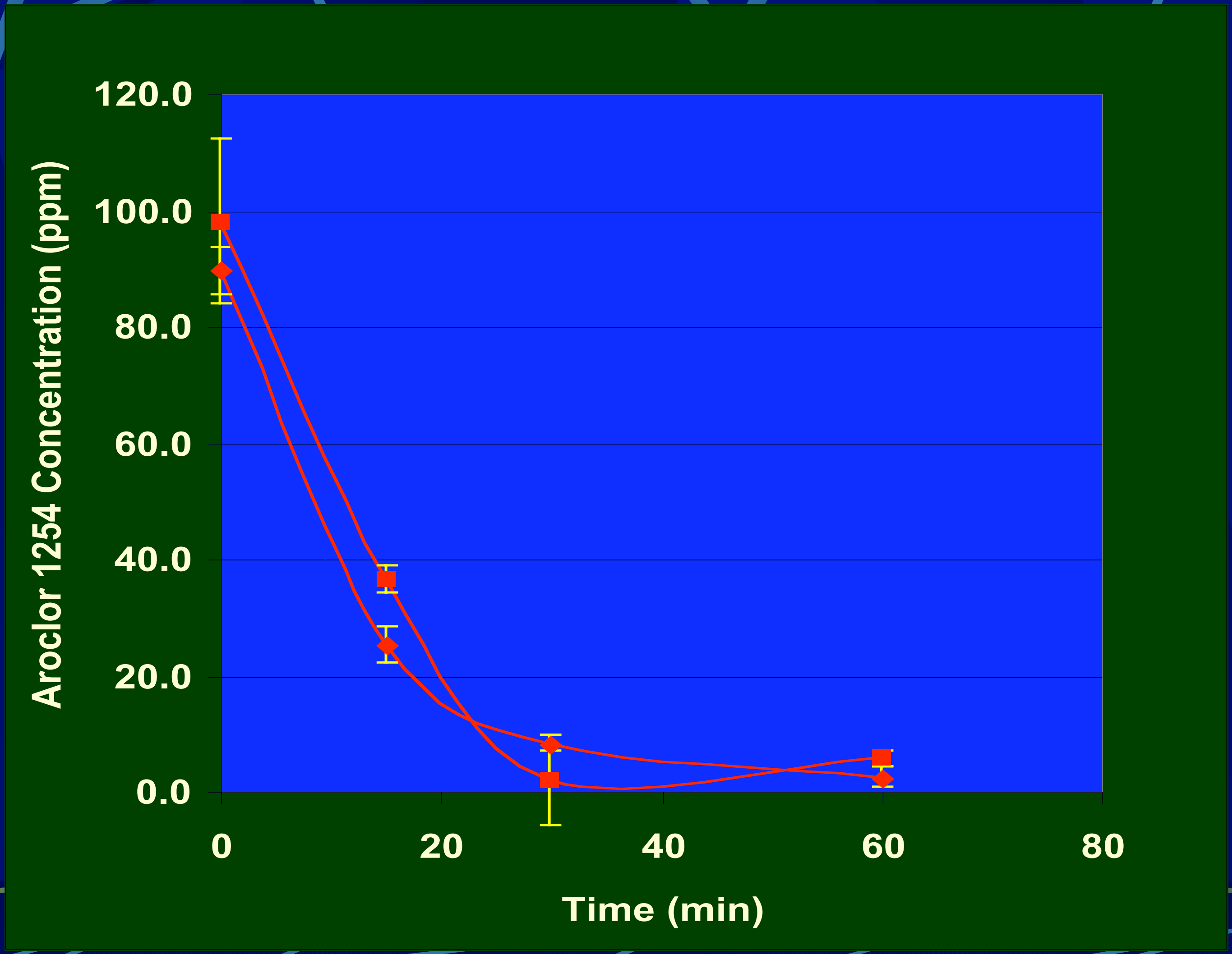


Results (Photodegradation of PCBs extracted from soil)

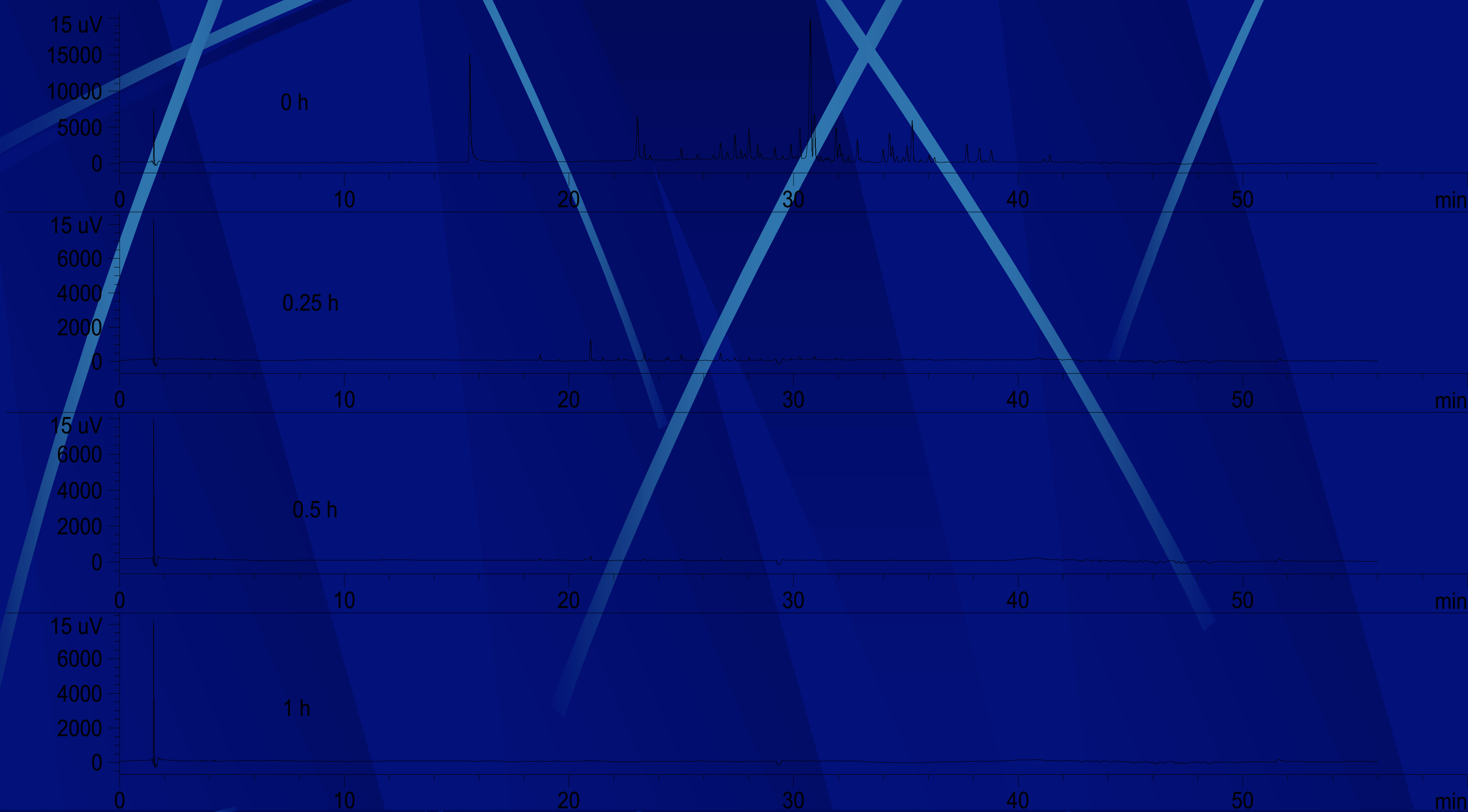
Photodegradation in 350 nm UV (with PT) in Alkaline IPA (different extractants/wash used)



Photodegradation of extract from wet soil using UV irradiation (350 nm),in alkaline (0.1N NaOH) IPA



Gas Chromatographs of wet soil extracts



Conclusions

- Photochemical degradation of highly chlorinated PCBs is a viable way to treat these hazardous compounds
- Solvent plays a significant role in photochemical degradation
- Photochemical degradation of highly chlorinated PCBs occurs fastest in alkaline IPA and when 254 nm UV light is used

Conclusions

- Biphenyls are also degraded using UV at 254 nm
- Use of Fenton's reagent decreases PCB concentration with time
- Use of photo-Fenton reactions for PCB degradation is feasible but requires more study
- Photochemical degradation (using 254 nm UV light) of soil extracts in alkaline IPA is a viable technology for remediation

Acknowledgements

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