

MONSOONAL AND POST MONSOONAL VARIATION IN THE ATMOSPHERIC LEVEL OF SELECTED ORGANOCHLORINE PESTICIDES (OCPs) IN PORTO NOVO, INDIA.

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Introduction

Organochlorine pesticides are still used in India for both agriculture and vector control. India's climate is dominated by monsoons. The agricultural, industrial, and economic productivity's in India is heavily dependent on the variability of the monsoon seasons. It is probable that the tropical climate facilitates the rapid dissipation of persistent organic pollutants (POPs) to air and water from agricultural areas of the tropics. POPs has been monitored in the past in various environmental media in and around Porto Novo, a fishing village in southern part of India, with levels much higher when compared to other studies of the world¹⁻⁴. Monsoonal and post monsoonal variation in the level of organochlorine pesticides (OCPs) was therefore observed in the atmosphere of Porto Novo using a high volume sampler, weekly, during 22nd June to 14th November-2006.

Materials and methods

Sampling

In the state of Tamil Nadu, Porto Novo (Lat. 11°26'30"N; Long. 79° 45'48"E), is mainly a coastal fishing village situated on the north bank of the mouth of the Vellar river in the southern part of India. During 22nd June-2006 to 14th November-2006, using a high volume sampler, weekly samples were collected.

Extraction

Prior to extraction a mixture of surrogate standards (2,4,5,6-tetrachloro-m-xylene (TCmX), deca-chlorobiphenyl (PCB209), ¹³C₁₂-PCB138 and ¹³C₁₂-PCB180) were added to each of the samples. The samples were Soxhlet extracted for 18 h with DCM. Activated copper granules were added to the collection flask to remove potential elemental sulfur. The extract was rotary evaporated and transferred with hexane to a 15mL amber vial. This was blown down under a gentle stream of nitrogen to about 0.5mL and cleaned on a 8 mm i.d. chromatography column with 6 cm alumina (BDH neutral Alumina 3% deactivated), 10cm of silica gel (Merck Silica 60 3% deactivated), 10 cm of 50% sulfuric acid silica and 1 cm of baked sodium sulfate (all baked at 450°C overnight) and the column was eluted with 10 ml mixture of 50:50 hexane: DCM (v/v). The samples were reduced to a final volume of 25µl after adding 25 µl of dodecane as solvent keeper and a known quantity of

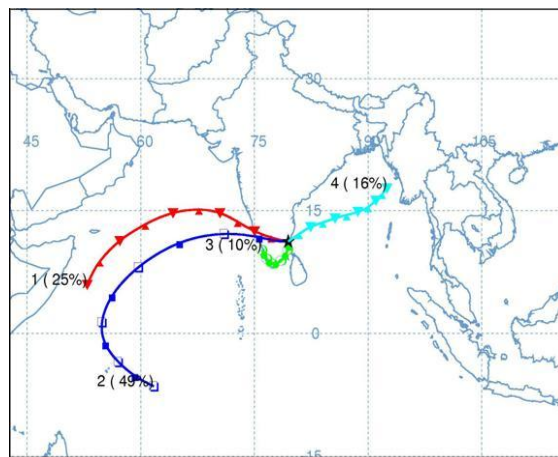


Figure 1. 5 Days mean back trajectory at Porto Novo, India

pentachloronitrobenzene (PCNB) and PCB-54 was added as an internal standard prior to GC-MSD analysis. OCPs analysis was carried out on a Finigan-TRACE GC-MS system with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 μ m), operating under single-ion monitoring (SIM) mode. Helium was used as the carrier gas at 1.2 mL min⁻¹ under constant-flow mode. The oven temperature began at 60 °C for 1 min and increased to 290 °C (10 min hold time) at a rate of 4 °C min⁻¹. Splitless/split injection of a 1 μ L sample was performed with a 5 min solvent delay time. Injector temperature was at 250 °C.

QA/QC

Chemical standards were purchased from Accustandard Co. U.S. Laboratory and field (i.e., samplers sent to/from field sites unopened) blanks consisting of pre-extracted PUF disks were extracted and analyzed in the same way as the samples. Analytical blanks consisted of six field and three laboratory blanks. There was no significant difference (*t* test significance, <95%) between analyte concentrations in the laboratory and field blanks, indicating contamination was negligible during transport, storage, and analysis. Surrogate recoveries were between 67% and 135%. Reported values were recovery and field blank corrected.

Result and Discussion

In order to assess the possible sources of OCPs using the HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, Version 4.7), a comprehensive modeling system developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory⁵. 5 Days mean back trajectories ending at Porto Novo at 0600 UTC, i.e. 11:30 local time for all sampling dates, were calculated (see Figure 1). In order to classify the air masses, the trajectories ended at the height of 500m AGL (above ground level), a level of about half the height of the mean day time planet boundary layer (PBL), to represent general transport conditions in the PBL.

Cluster 1(25%): The air mass of this cluster originated at the south-west of Arabian Sea crossing the southern states of Karnataka and enters Tamil Nadu and ultimately ends up in the sampling site at Porto Novo.

Cluster 2(49%): This air mass originated from the west of Indian Ocean and after traveling through the southern state of Kerela crossing the state of Tamil Nadu ultimately ends up at Porto Novo.

Cluster 3(10%): This parcel of air mass crossed the bordering limits of Karnataka, Tamil Nadu and ends up at Porto Novo.

Cluster 4(16%): After crossing the Bay of Bengal this mass of air parcel ends at Porto Novo.

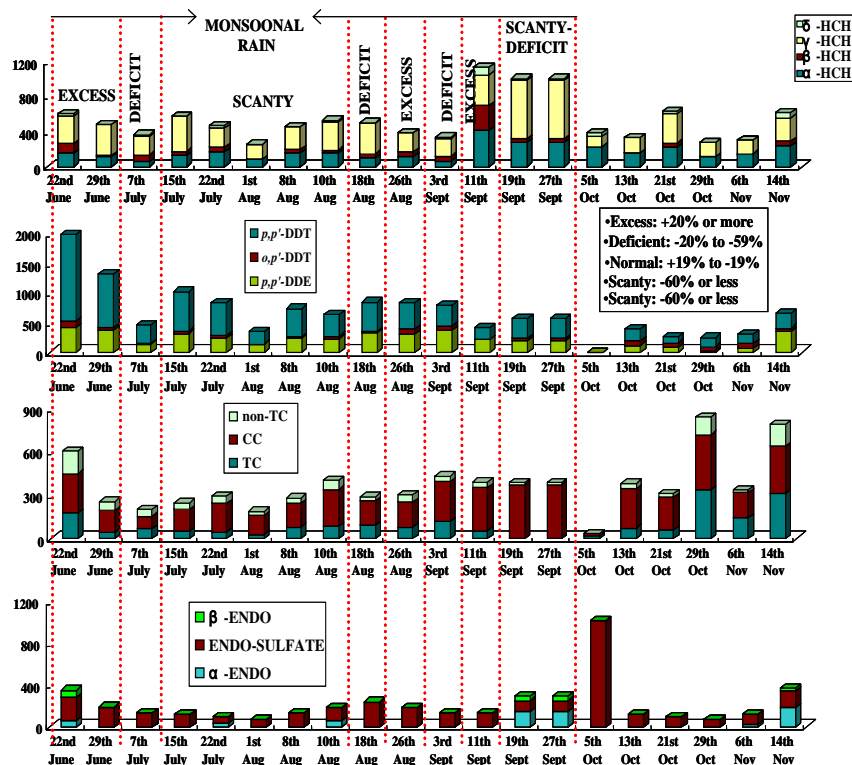


Figure 2. OCPs level during the monsoonal and post monsoonal phases in Porto Novo

HCHs

The range of total HCHs (i.e., sum of α , β , γ and δ isomers of HCH) in Porto Nova varied between 260-1135 (average 535) pg/m^3 . Highest level of all the four isomers of HCH observed on 11th September might be due to on spot application of technical HCH. Similar higher levels of HCHs has been observed at past^{1,2} though the level has slightly decreased and lower than other parts of India^{6,7}. But the level is higher than other parts of the world. Like most parts of India α/γ -HCH ratio in Porto Novo has been found to be below unity except on 11th September and 5th October the ratio was greater than one indicating the use of technical HCH on these two dates. The seasonal variation of HCHs and DDTs at Porto Novo, south India showed higher levels from August to January with marked HCH concentration during the rice cultivation season.

DDTs

The total DDT concentrations (Σ DDT, sum of p,p' -DDT, o,p' -DDT and p,p' -DDE) ranged from below the level of detection to 1980 pg/m^3 with an average of 660 pg/m^3 . The average concentration is close to Bangalore and Kolkata in a recent study but lower than other parts of the country^{6,7}. The highest level has decreased nearly three times than the last study at this site² may be due to the ban on the use of technical DDT for agricultural purpose. The p,p' -DDT dominated the congener pattern contributing about 60% of the total DDT concentration and is consistent with the recent PAS study on coastal length of India⁶. The o,p' -DDT/ p,p' -DDT ratio is close to technical DDT (technical DDT~0.3) in consistent with recent studies in India^{6,7}. The ratio varied 0.06-0.22 during the south-west monsoon period but the ratio increased (0.4-0.8) in the post monsoon period. This may be due to the use of DDT for vector control programs during monsoonal rains. High p,p' -DDE levels in most of the samples indicate past use of the compound. Withdrawal of monsoon may be the possible reason for no DDT level on 5th October. But the high o,p' -DDT/ p,p' -DDT ratio in the post monsoonal period signifies some illegal use in the agricultural field as the vapour density of o,p' -DDT is 7.5 times greater than p,p' -DDT⁸.

ENDOs

The overall range observed in the present study (pg/m^3) ranges 66-1015 (average 220). Endosulfan sulfate dominated the congener pattern contributing about 81% of the total concentration of endosulfans reflecting use of this compound in the past around the Vellar estuary⁹ and endosulfan sulphate is more persistent in the environment than its parent compounds. This range is lower than other parts of ^{6,7} and China¹⁰. Technical grade endosulfan comprises of two stereo isomers, α and β -endosulfan in a ratio of 7:3. In the present study the ratio is 1-6 (average 0.7) with α -endosulfan contributing 15% and β -endosulfan 4% of the total endosulfan. The ratio was 4 on 19th and 27th September and 6 on 14th November but the ratio was below 1 for rest of the samples. This reflects on spot application of endosulfan in the agricultural field on these dates.

CHLS

The three isomers of chlordane viz., trans-, cis-, and trans-nonachlor were detected and the total concentration of CHLs (*trans*-, *cis*-, *trans*- and *cis*-nonachlor) in pg/m^3 ranges between 36-840 (average 368). This range is much lower than other parts of India^{6,7} and Guangzhou, China but comparable to Hongkong⁸ in Asia. Unlike other parts of India^{4,5}, the cis isomer dominated the congener pattern contributing 61% slightly more than twice of the trans isomer (25%). Low TC/CC ratio (0-0.9,4 \pm 3) but with a higher total chlordane concentration implies that the high temperature in this tropical site is possibly initiated by the degradation of trans-chlordane¹¹.

HCB

HCB concentrations (pg/m^3) derived from this study ranged from 52-135 (average 81). The level was consistent during the monsoon but there was an elevation in the concentration in the post monsoon period with the highest level on 14th November.

Conclusion

The massive decline in the levels of DDTs and HCHs in Porto Novo from previous records indicates the recent ban on the technical mixture of these compounds for agricultural purpose though they are used for vector control programs. But possibly in some occasion technical HCH is still used in Porto Novo especially during paddy cultivation. DDT level is due to its usage for vector control.

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References

1. Baburajendran, R., Venugopalan, V.K., Ramesh, R., 1999. *Chemosphere*, 39(10): 1699-1706.
2. Ramesh, A. et al., 1989. *Environmental Pollution*, 62(2-3): 213-222.
3. Tanabe, S., Kunisue, T., 2007. *Environmental Pollution*, 146(2): 400-413.
4. Kannan, K., Tanabe, S., Ramesh, A., Subramanian, A., Tatsukawa, R., 1992. *J. Agric. Food Chem.*, 40(3): 518-524.
5. Draxler, R. R.; Rolph, G. D. *NOAA Air Resources Laboratory, Silver Spring, MD* . (2003). Available at: <http://www.arl.noaa.gov/ready/hysplit4.html>.
6. Zhang, G., Chakraborty, P., Li, J., Sampathkumar, P., et al., 2008. *Environ. Sci. Technol.*, 42 (22): 8218-8223.
7. Chakraborty P., Zhang, G., Li, J., Xu, Y., Liu, X., Tanabe, S., Jones, K. C. 2010. *Environ. Sci. Technol.* 44: 8038-8043.
8. Spencer, W. and Cliath, M.M., 1972. *J. Agric. Food Chem.*, 20(3): 645-649.
9. Rajendran, N., Venugopalan, V.K., 1991. *Bulletin of Environmental Contamination and Toxicology*, 46(1): 151-158.
10. Li, J.;Zhang, G., Guo, L. L., Xu, W., Li, X. D., et al., *Atmospheric Environment*. 2007; 41, 3889.
11. Halsall, C.J. et al., 1998. *Environmental Pollution*, 102(1): 51-62.