



### B84 Screening of Phenoxy Acid Herbicides in the Everglades and Biscayne Bay National Parks: A Concern of Environmental Forensics

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The goal of this presentation is to present to the forensic community the capabilities and advantages of using a combined SPE/LC/MS method as an analytical tool for monitoring the presence of phenoxy acid herbicides in sediments with high content of organic carbon.

Environmental forensic scientists and investigators have the challenge to answer questions such as: Who caused the contamination? When and how did the contamination occur? Was it an accidental spill or a series of routine releases? Is there a chronic source responsible for the background concentrations observed? Are the results reliable both in terms of the detection limits and identification of the contaminants? However, none of these questions can be satisfactorily answered with the lack of validated and sensitive analytical and statistical methods as well as a preliminary knowledge of the baseline levels of the analytes of interest.

The presence of pesticides in the environment has created an increased concern over potential health hazards associated with its exposure in different environmental matrices such as air, water, sediments, and in some instances fish tissue samples (which can be used as an indicator of the bioaccumulation of toxic chemicals through the food chain).

Based on limited published information it appears that sediment/soil, water, and biota in South Florida often contain low concentrations of a variety of inorganic and organic contaminants including formerly and presently used pesticides. However, there are still large data gaps regarding the occurrence and distribution of these contaminants in particular along sensitive ecosystems such as the Everglades, Biscayne, and Florida Bay despite their close proximity to places such as the Homestead Agricultural Area.

As a response to that need, and in preparation for the major changes that will be introduced by the CERP (Comprehensive Everglades Restoration Plan), selected sections of Everglades National Park are currently being surveyed for a series of organic and inorganic contaminants. The data presented here is focused in the development of a sensitive method for the analysis of phenoxy-acid herbicides with particular emphasis in complex sediment matrixes such as organic rich sediments (i.e., peat).

The chlorinated phenoxy acid herbicides were introduced in U.S. in the mid 50s as defoliants mainly to eradicate weeds. Since that time, some of these pesticides have been prohibited or restricted or reformulated because of their linkage with more toxic substances like chlorinated dioxins and furans.

The analytes of concern are: 2,4-D, 2,4,5-T, acifluorfen, 2,4,5-TP (silvex), Picloram, Mecoprop (MCPP), 2,4-DB, Bentazone, Dicamba, Dichlorprop, Dinoseb, and MCPA.

The method presented here is a combination of solid phase extraction over graphitized carbon of a water extract of the sediment sample. Key advantages of the method over regular liquid-liquid extractions are the reduction of organic solvents used as well as the natural compatibility of aqueous samples with LC/MS.

The cleanup procedure was as follows: the sediments samples were extracted using 100 mL of NaOH 0.3 N, and sonicated for 30 minutes. They were filtered using a Buchner funnel in vacuum and then transferred to a 1 L flask. The pH was adjusted and deionized water added *qs* to 1000 mL. In order to avoid the precipitation of fulvic/humic acids, an additional filtration step was performed using 0.45  $\mu$ m filters. The samples were loaded in the pre-conditioned Carbon-based SPE cartridges at a flow rate of 20 mL/min. Two fractions were collected during the elution step, using 1.5mL of MeOH and 13mL of a fresh solution of CH<sub>2</sub>Cl<sub>2</sub>:MeOH:TFA (80:20:0.2%) respectively. The fractions were concentrated up to 200 $\mu$ L under nitrogen and then mixed prior to injection into the LC/MS system.

A Finnigan Navigator LC/MS from Thermo Quest was used with SIR mode for all analytes. The ESI source was operated in negative mode (ESI-), with an optimized cone voltage of 15 V. The gradient elution was performed in a Zorbax XDB C<sub>18</sub> Column (250 x 4.6 mm x 5  $\mu$ m) using MeOH and HOAc 1% as modifier from t = 0-15 min at 75:25 (MeOH:HOAc 1%) through 82:18 until 25 minutes as total run time. A linear response for the quantitation ( $r^2=0.99$  or better) was obtained at the concentrations of interest using 2,4-dichlorophenoxyacetic-acid as internal standard. The limit of detection (LOD's) for the aforementioned pesticides in spiked sediments ranging from 100 ng/g to 300 ng/g.

Sediment samples from different zones of interest in the Everglades and Biscayne Bay National Parks were analyzed and the results are also presented.

#### Herbicides , Environmental Forensics, LC/MS