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Subject: Revised Extended Outline
Date: Thu, 20 Apr 2000 15:56:30 -0400
From: "Curtis Pollman" <cpollman@worldnet.att.net>
To: "Garth Redfield" <gredfiel@sfwmd.gov>
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Garth:

Here is the revised outline that earlier this morning I said I would forward to you. Apart from editorial changes, the only substantive changes were (1) the deletion of the fourth objective - scaling the measured P deposition fluxes to the entire Everglades - this objective of course is a Phase III-type study; and (2) elimination of throughfall studies at the satellite studies.

The throughfall study site will have considerable replication to characterize the within site variability we believe will occur. Ergo, we do not believe that it will be feasibleduring Phase II to extend the scaling study beyond the Primary site to the Satellite sites . It also is important to note (although I do not state so in the outline) that, under ideal circumstances, we believe the throughfall work should span three years:

- **Year 1 (Phase II)** - Conduct four (quarterly) 10-14 day intensive dry deposition and throughfall sampling experiments in a single 20m x 20m sawgrass plot in LNWR. Evaluate all sampling and analytical methods for appropriateness and accuracy.
- **Year 2** - Conduct additional 10-14 day intensive dry deposition and throughfall sampling experiments on 2-3 additional representative Everglades vegetation types in LNWR (for example, Typha stands and tree islands). Continue to evaluate and calibrate sampling and analytical methods, searching for sampling methods that are amenable to long-term, unattended deployment.
- **Year 3** - Identify "best methods" for sampling and analysis, and expand sampling program to representative vegetation types in central and southern Everglades. Conduct periodic intensive experiments to develop and calibrate sampling and analytical methods.

Since Phase II by definition includes 12 months of monitoring only, we are of course only proposing the Year 1 field work as part of the Phaes II Workplan.

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Subject: Final Outline for Phase II
Date: Thu, 27 Apr 2000 12:21:25 -0400
From: "Curtis Pollman" <cpollman@worldnet.att.net>
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Garth:

Here is the final version of the extended outline for Phase II (i.e., Task 6). We have considered and addressed all your comments in our revisions. Please note, however, our response to the following questions you raised:

Question to EPDP team: During field campaigns, are you planning on short-term deployment at more satellite sites to look at gradients and spatial aspects of special events??

Answer: No. The intensive field campaigns will focus on the Primary site only due to logisitic constraints. We are adding routine wet deposition to the satellite sites but we are of course concerned with avoiding bird excrement problems. We recommend daily visits to the sites where wet deposition is being collected so that the sampler can be cleaned when necessary, and so we don't lose entire (week-long) samples due to one bird dropping on one day out of 7. For this to be feasible, we would need the District to commit a staff person or two part-time to conducting daily site servicing. Are you guys willing to do that?

Gradient and spatial definition will be an important part of Phase III, should the District decide to move forward with the study once we complete PhaseII. We do not believe we can do an acceptable monitoring program to accomplish this in Phase II, although we certainly are interested in looking at gross gradients with the NRI. The design of a Phase III air monitoring network would include definition of variations in space and time with intensive monitoring at various sites. Note also that (a) special events are too hard to predict and (b) logistics too difficult to work out to mobilize efficiently and effectively. This is not to say that we feel these information are not worthwhile; indeed we believe that special event info would be very useful. As Steve Lindberg has noted, perhaps the so-called 80/20 rule that seems so often to apply in nature will also apply here, *viz.* 80% of the deposition may occur during 20% of the events.

Question: *Let's avoid too much investment splitting hairs with the MOUDI at less than 10 um. Wouldn't two or three size classes in this interval get the job done?*

We believe we need to measure aerosols below 10 um in 10 stages because much of the world including NOAA believes that the fines predominate. If we do not measure fines then we will not have an acceptable modeling application study. We can use Anderson samplers instead of MOUDI because Bill Landing has them already. Kne Noll, however, does NOT recommend this because (1) the MOUDI rather than the Anderson is the state-of-the art; and (2) the MOUDI is deemed a much better collector for the many reasons Ken outlined in the Task 1a report.

The real costs of course lie in the number of samples that need to collected and not in the purchase of the sampler. We can, however, composite samples to save costs. We can composite by size and also by sample combination, a procedure Ken has done in the past. We will certainly explore this as we pin down the number of samples to be collected, and the individual sample costs, etc. The preparation of the sample surfaces for collection and weighing is also low per sample after the operation is set up and becomes routine or rote

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Phase II

Atmospheric Deposition Phosphorus in the Everglades: Proof of Concepts and Methods

Extended Outline

Introduction

The greatest uncertainty in our understanding of the atmospheric fluxes of phosphorus to the Everglades concerns rates of dry deposition, which may account for 50% of the total atmospheric flux. The best available evidence suggests that 90% of the dry deposition flux of phosphorus derive from so-called giant particles which tend to peak in size distribution around 20 μm in diameter. Given the current state-of-the-art, we should be able to reduce the uncertainty in dry deposition rates of phosphorus by ± 2x. Our field program is designed to bound and reduce this uncertainty using flat plat measurements and appropriate models to establish the lower limits of deposition, and use total throughfall measurements coupled with litterfall to establish the absolute upper limit (Figure 1).

Objectives

The overall objective is to develop a method for estimating the dry deposition P flux that is amenable to routine deployment and that gives reliable, reproducible flux estimates that can be calibrated to estimate total P flux to the various Everglades canopies. In order to achieve this overall goal, the following study objectives can be defined:

1. Constrain Fluxes – Establish upper and lower limits of dry deposition of phosphorus that are reasonably well constrained.
2. Intercompare Methods – Develop a consistent, defensible, reliable method for measuring the flux of P to a smooth surrogate surface. These methods have been well calibrated and will give us a lower bound.
3. Calibrate Fluxes to a Vegetated Canopy – Develop a "ground-truth" method to produce a scaling factor that will enable us to relate fluxes derived from surrogate surface measurements and ambient aerosols to actual canopy deposition.

Experimental Design

The experimental program will involve conducting flux measurements using three fundamentally different techniques to bound the upper and lower limits of P dry deposition rates (Figure 2). Flux estimates will be derived from ambient aerosol measurements, fluxes to surrogate surfaces, and from throughfall measurements. Sampling will consist of two components: intensive and routine monitoring. Field measurements during Phase II are anticipated to span a full 12 months. At the conclusion of the 12 month monitoring period, the Tetra Tech team will prepare a report detailing the results of the study, including an analysis of how well the different techniques used in the study are measuring P dry deposition fluxes.

Primary Site

A single site (the Primary Site) will be heavily instrumented to conduct the methods intercomparison. Experiments conducted at the Primary Site will include both routine monitoring and a series of intensive experiments both to examine how well different methods compare and to establish the correlation between flux estimates derived from well-characterized aerosol measurements and from surrogate surface measurements. The Primary Site must be readily accessible, and will require security, AC power, direct access to the marsh, and ideally will have a high phosphorus dry deposition signal. The headquarters for the Loxahatchee National Wildlife Refuge appears to be the leading candidate for the intensive site, although the SFWMD's ENR site is another candidate site. Equipment at the intensive site will be tower-based, and will be instrumented with routine meteorological equipment so that it mirrors the NOAA Coastal Margins study Florida Bay site, thus facilitating NOAA participation and validation of their flux measurements.

Instrumentation for routine monitoring at the intensive site will include or measure:

- Filter packs
- Dichotomous samplers
- Frisbee sampler and British reversed Frisbee sampler
- Wind speed and wind direction
- Standard PM_{10}
- Eagle dry deposition sampler (long-term)
- Scaling factor studies (throughfall) (conducted quarterly)
- Wet deposition
- Water surface collectors

We propose conducting 10 "ambient air" intensive study campaigns during the 12-month time frame of Phase II. The duration of the ambient air intensive campaigns likely will be 3 to 5 days. Coincident with four of the ambient air intensive experiments, we also will conduct a set of quarterly intensive throughfall experiments (see next section on throughfall experiments). The timing of the 10 ambient air intensive sampling campaigns over 12-month period will be designed to capture the full dynamic range of meteorological conditions and terrestrial impacts (e.g., Saharan dust outbreaks, pollen blooms). Instrumentation and measurements to be used or conducted during the ambient air intensive campaigns will include:

- Wet deposition (event sampling during intensives)
- MOUDI – 10 stage particle size cut from 0 to 10 μM
- Noll Rotary Impactor
- Individual, manually loaded flat plate samplers

Table 1 summarizes the instrumentation, the sampling schedule, and the parameters measured at the Primary Site.

Satellite Sites

Satellite sites will be used to examine the influences of expectedly different wind regimes and source regions for aerosol P. In conjunction with the Primary Site (LNWR), satellite sites (e.g., Belle Glade, ENR, S-9/FEDDS site) will yield a north-south gradient to begin examination of different aerosol P sources. Satellite sites will consist of an unattended Eagle dry deposition sampler on an anticipated 15-day sampling regimen. The integration period will be adjusted to ensure collection of detectable levels of aerosol P. Four Mylar strips will be collected, two utilized for chemistry, one for light microscope counting, and one will be archived. Table 2 summarizes the instrumentation, the sampling schedule, and the parameters to be measured at the Satellite Sites. Archived flat plate samples can be selectively identified based on measured loading and meteorological data for subsequent individual particle analysis using scanning electron microscopy. We also will conduct other major and trace element analyses routinely on samples analyzed for total P.

Throughfall Studies

Throughfall studies will be conducted to help constrain and "ground-truth" estimates of P dry deposition (Figure 1). Ground-truthing refers to developing a factor that will enable us to scale P deposition measured with surrogate surfaces, and calculated from ambient aerosol sampling, to account for deposition to the canopy. The general approach is, in essence, to develop a "mass-balance" coupled with an "inert" dry deposition tracer (Na^+) to calculate P dry deposition.

The following mass balance equation applies for the dry deposition flux for any chemical species:

Throughfall (TF) + Stem Flow (SF) = Rainfall deposition (R) + Aerosol Dry Deposition Washoff (DD) + Foliar Leaching (FL)

FL may be either positive or negative, and would be extremely difficult to measure accurately for phosphorus. There is, however, ample evidence that foliar leaching (FL) is negligible for sodium cation; thus we can determine aerosol dry deposition (DD) of sodium from field measurements of TF, SF, and R:

$$DD_{Na} = SF_{Na} + TF_{Na} - R_{Na}$$

Previous research supports the contention that the P/Na ratio in aerosols and/or aerosol dry deposition captured using surrogate surface techniques reflects what is dry depositing to various Everglades vegetation and surfaces. thus, we can calculate aerosol P dry deposition from DD_{Na} and the P/Na ratio in ambient aerosols and/or aerosols captured with surrogate surface sampling methods:

$$DD_P = DD_{Na} \times (P/Na)_{DD}$$

Throughfall Measurement Program

Throughfall samples will be collected on an event basis, or integrated for ≤ 24 hours in order to: (1) minimize sample storage artifacts; (2) minimize impacts from bird excrement; (3) assure that recently dry-deposited aerosols come from the same aerosol population as the those washed out with the rainfall.

The throughfall measurement program for Phase II will focus on measuring deposition rates to a major Everglades canopy type, *viz.* sawgrass. We will identify a suitable, accessible sawgrass marsh at the Primary Site to establish a 20m x 20m test plot. The following regime of collectors will be deployed (Figure 3):

- Deploy 4 wet-only rain collectors at the corners of the plot.
- Deploy ≥ 15 throughfall collectors at the base of the sawgrass stems, above the water surface.
- Deploy stem-flow collectors on individual sawgrass stems.
- Deploy various surrogate surface dry deposition collectors at (very) nearby site.

We propose to conduct four (quarterly) 10-14 day intensive dry deposition and throughfall sampling experiments in a single 20m x 20m sawgrass plot at the Primary Site. The timing of the throughfall experiments will be coordinated to correspond to the timing of the ambient air intensive experiments. As part of the throughfall experiments, we will evaluate all sampling and analytical methods for appropriateness and accuracy.

Throughfall Analytical Methods

Additional experimental methods will be tested in an effort to lower detection limits for P and the trace metals, and to increase the number of trace elements that can be measured on each sample. The Finnigan "Element" high-resolution magnetic sector ICP-MS at FSU has been proven to agree with standard EPA methods for total dissolved P, but offers a 10-fold lower detection limit. The ICP-MS also will be used to conduct analyses for Na, as well as other trace elements of interest (e.g., Ca, Mg, and K in wet deposition). Any experimental methods will be carefully compared with EPA-approved methods, using QA/QC procedures that are consistent with our approved SOPs.

Timeline and Key Deliverables

The timeframe of Phase II is expected to span approximately 24 months. The first three months following the execution of the Contract Amendment will be devoted to equipment acquisition and fabrication. Following the initial three month initiation period, the field research and monitoring program will begin for a period of 12 months. At the conclusion of the field research and monitoring program, the Tetra Tech team will produce or achieve the following:

- Quality-assured data set, including descriptive narratives of the methods (due by Week 72 of Phase II)
- Data analysis and interpretation, including a discussion of the strengths and limitations of the methods and results (due by Week 80 of Phase II).
- Develop a plan for producing a suite of manuscripts to be submitted to peer-reviewed journals (due by Week 90 of Phase II)
- Develop suite of manuscripts to be submitted to peer-reviewed journals (due by Weeks 92 - 104 of Phase II)
- Demobilization and termination of project (Week 104).

Table 1. Proposed instrumentation, sampling schedule, and parameters to be measured at the Primary Site.

Instrument	Comments
MOUDI	10 size cuts; perhaps run a replicate MOUDI during a single intensive. Samplers run 3 to 5 days. Filters are pre- and post-weighed. Analyze for total P using high-resolution magnetic sector ICP-MS. Can get ca. another 30 elements for source characterization.
Noll Rotary Impactor	8-hour and 16-hour sampling regime, run initially 2 NRI's in replicate. Each sampler has 4 foils that need to be weighed and extracted for total P – no archiving, splitting or counting.
Dichotomous sampler	Operate at the same schedule as the MOUDI.
Filter Pack	Weekly integrated; two samples – total, and $PM_{2.5}$. P speciation likely.
Davidson Frisbee and reversed Frisbee	Measure total P
Water surface collector	Measure total P
PM_{10}	24 hours integrated sampling – weigh and extract sample for total P
Eagle	15-day sampling regimen. Four Mylar strips collected, two utilized for chemistry, 1 for light microscope counting, and 1 for archival.
Throughfall – Canopy Scaling	Canopy scaling network will be operated on a time scale compatible for direct comparison of results with those from Eagle dry deposition sampler.
Aerochemetrics wet/dry collector	Weekly integrated wet deposition samples collected on NADP/NTN schedule. Analytes include total phosphorus, all major cations and anions, including NO_3^- and NH_4^+, and specific conductance. The latter components are included to help identify analytical problems and possible contamination.
Manual Plates	8-hour day/16-hour night sampling. Sample mass weighed, conduct chemistry and count particles.

Table 2. Proposed instrumentation, sampling schedule, and parameters to be measured at the Satellite Sites.

Instrument	Comments
Eagle	15-day sampling regimen. Four Mylar strips collected, two utilized for chemistry, 1 for light microscope counting, and 1 for archival.
Aerochemetrics wet/dry collector	Weekly integrated wet deposition samples collected on NADP/NTN schedule. Analytes include total phosphorus, all major cations and anions, including NO_3^- and NH_4^+, and specific conductance. The latter components are included to help identify analytical problems and possible contamination.

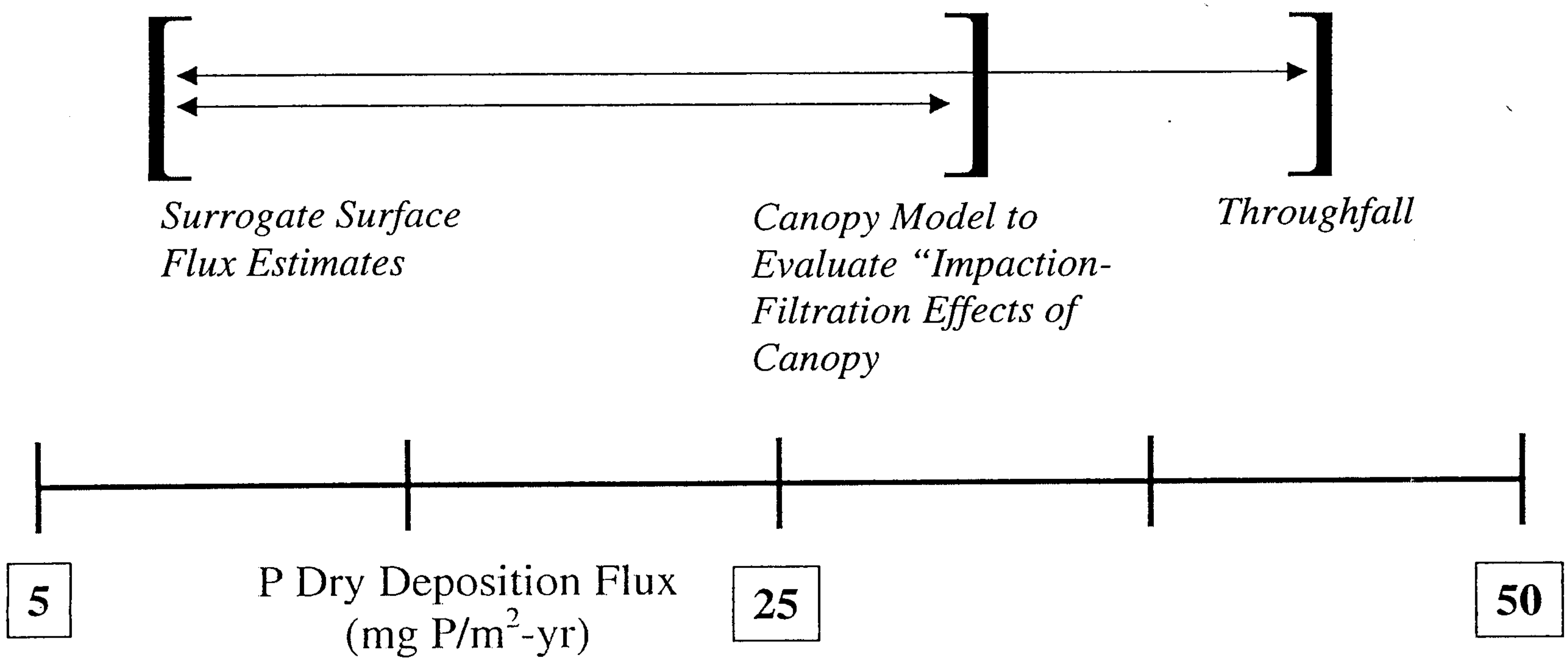

Figure 1. Schematic diagram of proposed experimental program illustrating project goal to increasingly constrain the possible upper & lower bounds for aerosol P dry deposition.

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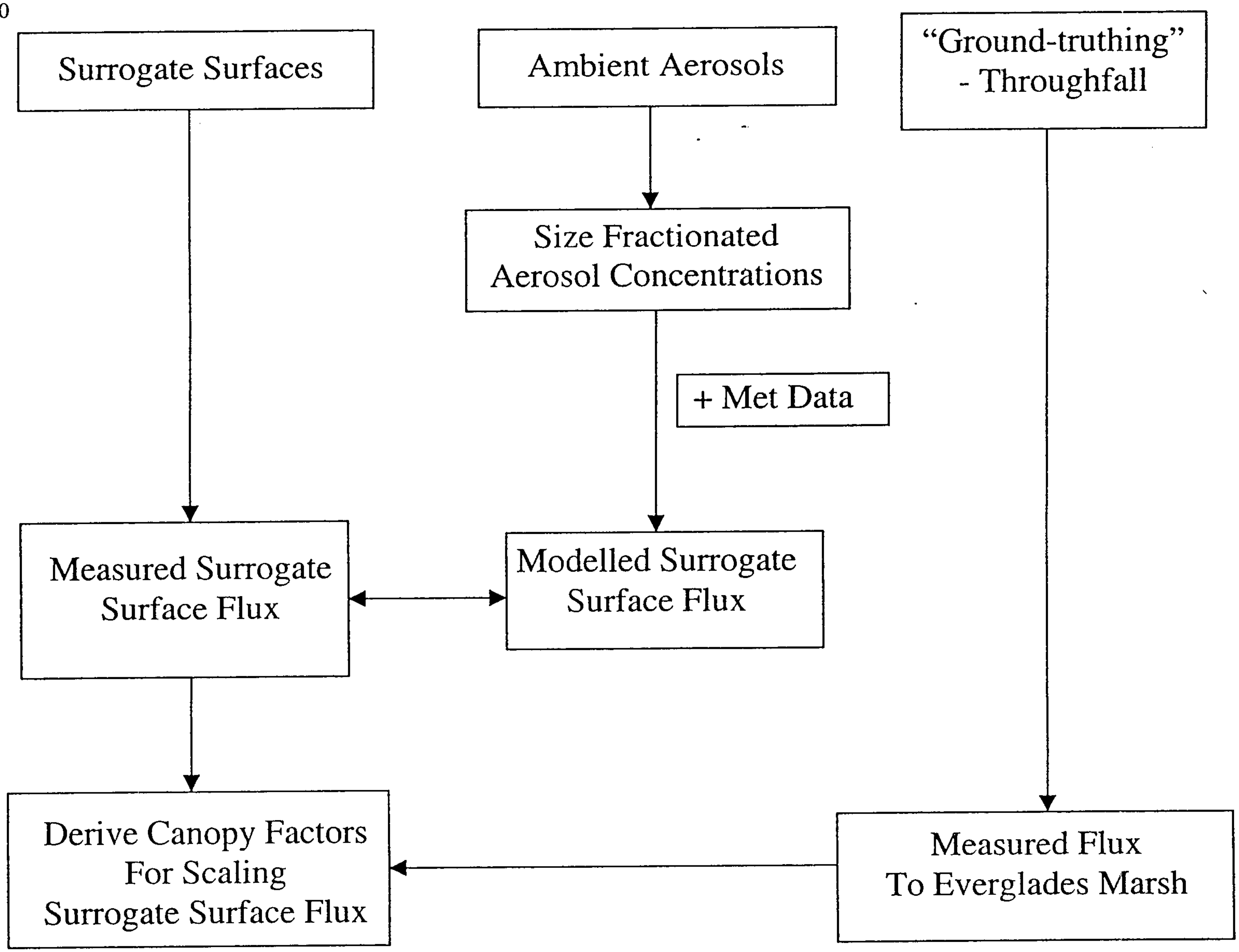

Figure 2. Schematic diagram illustrating the three basic measurement components of the proposed overall experimental design.

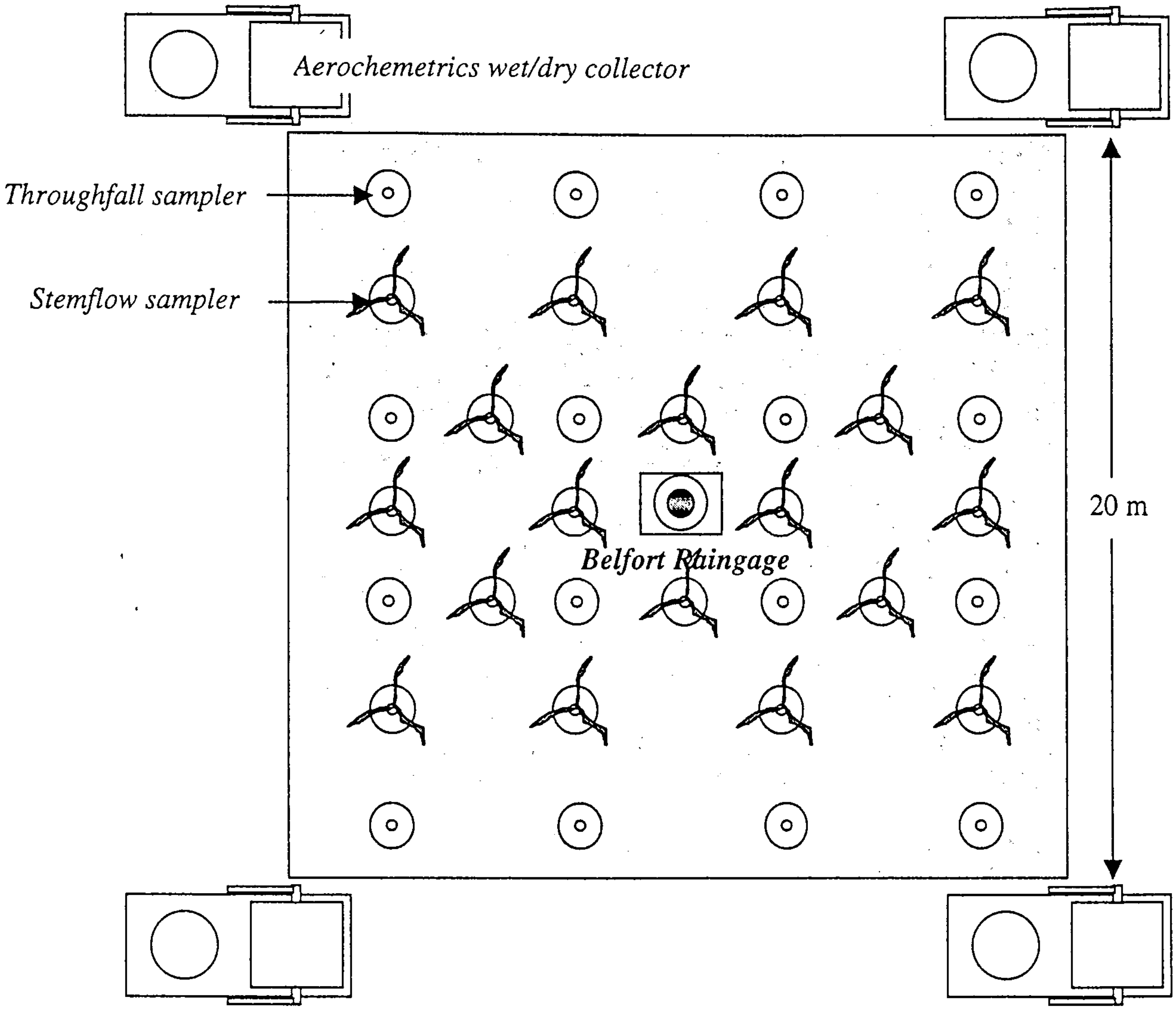

Figure 3. Schematic diagram illustrating collector configuration and instrumentation at the *Cladium* (sawgrass) throughfall experimental plot located at the Primary Site. Plot will encompass 20 m x 20 m, and will include four Aerochemetrics wet/dry collectors deployed just above the top of the sawgrass canopy and a Belfort recording raingage. In addition, 16 throughfall collectors consisting of 181 cm^2 funnels connected to 1L receiving bottles will be deployed just above the water surface. Stemflow will be measured using 18 stemflow collectors attached to sawgrass.