



Atmospheric Environment 33 (1999) 5123-5131

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Outlier detection in phosphorus dry deposition rates measured in South Florida

Hosung Ahn^{a,*}, R. Thomas James^b

"Water Resources Evaluation Department, South Florida Water Management District, 3307 Gun Club Road, West Polm Beach, FL 33406, USA

^bEcosystem Restoration Department, South Florida Water Management District, 3301 Gun Club Road, West Palm Reach, FL 33406, USA

Received 2 September 1998; received in revised form 6 February 1999; accepted 15 February 1999.

Abstract

Dry atmospheric deposition contributes a significant amount of phosphorus to the Everglades of South Florida. Measurement of this deposition is problematic, because samples often are contaminated to varying degrees by bird droppings and other foreign materials. This study attempted to detect and remove the outliers in phosphorus (P) flux rates measured from dry deposition samples. Visual inspection of the samples, recorded in field notes, found that 30.1% of the samples contained animal droppings and frogs. Some of the samples with droppings and frogs (2.3%) had P values greater than $884 \ \mu g P m^{-2} d^{-1}$ (a value twice the standard deviation of the raw data mean), and were removed from further analysis. Outlier detection statistics based on a linear regression were then used for additional data screening. Eight stations in the network of 19 were removed because high contamination precluded the use of the regression model. Of the remaining samples, 15.7% were identified through the regression procedure as contaminated and were removed. The 11 station mean for P dry deposition was $85.8 \pm 79.0 \ \mu g P m^{-2} d^{-4}$, prior to the regression analysis, and $74.8 \pm 75.1 \ \mu g P m^{-2} d^{-1}$ after removal. Published by Elsevier Science Ltd.

Keywords: Atmospheric deposition: Sample contamination; Environmental statistics; Linear regression; Quality control; Bird dropping

1. Introduction

Anthropogenic phosphorus (P) loads to the Everglades of South Florida have resulted in significant changes to this oligotrophic ecosystem (Davis, 1994). As a result, the State of Florida enacted a program to reduce P loading to the Everglades through a series of best management practices and large constructed wetlands known as storm water treatment areas (State of Florida, 1994). To manage these P loads, accurate monitoring and analysis are required of both controllable and non-controllable sources. In South Florida, where most water bodies are large and shallow, atmospheric deposition, a non-controllable source, is a significant contributor of P (Redfield, 1998). Therefore, the South Florida Water Management District (District) has been collecting wet/dry deposition samples in the region since 1987. As controllable loads from agricultural regions are reduced, atmospheric deposition will become even more significant.

Atmospheric deposition is commonly sampled in two separate forms: wet (rainfall) and dry (dustlall). Techniques for estimating dry deposition include methods of: micrometeorology; surface accumulation; throughfall; watershed mass balance; and inferential technique (Erisman et al., 1994). The District has used the surface accumulation method based on dry buckets to measure dry atmospheric deposition. The dry bucket method is simple, inexpensive, and, therefore, commonly used in field. In particular, this method is useful for measuring deposition of large particles (Hicks, 1986; Erisman et al., 1994). Since P is primarily associated with particles greater than 2 µm in diameter (Graham and Duce, 1982;

$$WRE - 365$$

^{*} Corresponding author. Tel.: +1.561-6876516; fax: +1-561-6876442.

E-mail address: hosung.ahn@sfwmd.gov/hahn@sfwmd.gov (11. Ahn)

^{1352-2310/99/\$-}see front matter. Published by Elsevier Science Ltd. PH: 81352-2310(99)00165-X

Lawson and Winchester, 1979), the dry bucket may be adequate samplers of P dry deposition.

Because most of the monitoring sites are located at or near marshes, contamination of dry deposition samples is very common. The major sources of contamination are bird droppings, body parts of insects and animals, dirt and dust, ash, and vegetation debris. These contaminants result in positively biased P values, which in turn bias the computation of summary statistics of the P loads.

Many sources contribute to dry deposition. These include a combination of oceanic acrosols, agricultural practices, burning, soil erosion, industrial and automobile pollution, vegetation, etc. (Redfield, 1998). Two concerus exist with these potential sources of contamination. The first concern is the origin of the contamination. If it is from inside the area of interest, then it is a contamination source, such as localized dust, frogs, bird droppings, vegetation, insects. If it is from outside the area of interest, such as some ash, dusts and vegetation debris, then it is a true part of the dry atmospheric deposition. It is almost impossible to determine the origins of these materials. The second concern is the impact that these sources may have on the estimates of P loads. If they add large amounts of P (such as bird droppings) then they tend to bias the estimate. If they add very little P (such as insect parts) then there is no contamination problem. The difficulty is to remove the bias (noise) while retaining the sienal.

This study presents a methodology to detect the outliers in the data for estimating the P flux rates from atmospheric deposition. This two-step approach identifies outliers of P flux in dry deposition samples by identification of contaminated samples through field note observations followed by a statistical analysis of the data using an appropriate regression technique. As far as the authors know, this is the first application of this technique for atmospheric dry deposition. This technique should be applicable to any atmospheric deposition measurement program, because it is a statistically valid method that can be used to remove extreme values from any data set.

1.1. Outlier detection techniques

Outliers are data that appear to deviate markedly from other members of the sample group in which they occur (Beckman and Cook, 1983; Barnett and Lewis, 1984). In relation to statistical analyses, Rousseeuw and van Zomeren (1990) defined outliers as observations that deviate from the estimates by a statistical model suggested by the majority of a data set. The latter definition implies that, in order to detect outliers, a statistical model can be used to define the residuals between observation and estimation, and the residuals can then be used to indicate aberrant data. There are a variety of statistical methods for detecting outliers (Barnett and Lewis, 1984; Beckman and Cook, 1983). One method is to set an outlier bound at either two- or three-standard deviations from the mean. However, with a limited number of samples, as is the case in most environmental monitoring, good estimates of population statistics cannot be obtained and the reliability of this simple method is uncertain. Statistical modeling approaches are more promising for detecting outliers than methods that rely on population statistics.

Statistical modeling methods include linear regression (Beckman and Cook, 1983), multivariate analysis (Roussecuw and Van Zomeren, 1990), and time series analysis (Beckman and Cook, 1983; Tiwari and Dienes, 1994). The multivariate method is not adopted here because 24% of the P deposition samples are randomly missing. These missing samples reduce the number of paired data sets, reducing the power of this technique. Preliminary analysis revealed a weak serial correlation of these P deposition data sets, making the time series analysis also inappropriate for the data. Thus, only linear regression methods were considered here.

The linear regression approach detects outliers by forming a clean subset of data that contains no outliers, fitting the regression for the clean subset, and testing for outliers relative to the clean subset based on test statistics. In this approach, the Studentized residuals are often used to test multiple outliers (Beckman and Cook, 1983). Finding a clean subset from a given data set is not trivial. The clean subset should produce, among all possible subsets, the smallest residual sum of squares. To find the clean subset having a size of *i* from a sample data set having a size of *n*, it is necessary to fit a regression model to each of the (i) possible subsets (where (:) is the number of combinations) and to find the minimum residual sum of squares. This method requires extensive computations that may not be feasible for a large *n*.

Three approaches are commonly available for finding a clean subset more effectively: a random search algorithm (Rousseeuw and van Zomeren, 1990); a forward search algorithm (Hadi and Simonoff, 1993; Atkinson, 1994); and a sophisticated elemental set algorithm (Hawkins and Simonoff, 1993). The forward search algorithm suggested by Hadi and Simonoff (1993) was used here since it is relatively simple and efficient computationally for finding a clean subset (Atkinson, 1994).

To introduce Hadi and Simonoff's Studentized residual, let us assume that a data set having a size of n is fitted by a simple regression model as

$$Y = X\beta + c \tag{1}$$

where Y is an *n*-vector of responses, X is an $(n \times k)$ matrix representing k explanatory variables with a rank of $k < n, \beta$ is a k-vector of regression parameters, and residuals e is a Gaussian random noise vector of size n with

$$d_{i} = D_{i}/\sigma_{M} = |\mathbf{y}_{i} - \mathbf{x}_{i}^{\mathrm{T}}\beta_{M}|/[\sigma_{M}\sqrt{1 - \mathbf{x}_{i}^{\mathrm{T}}(\mathbf{X}_{M}^{\mathrm{T}}\mathbf{X}_{M})^{-1}\mathbf{x}_{i}}],$$

if $i \in M$,
$$= |\mathbf{y}_{i} - \mathbf{x}_{i}^{\mathrm{T}}\beta_{M}|/[\sigma_{M}\sqrt{1 + \mathbf{x}_{i}^{\mathrm{T}}(\mathbf{X}_{M}^{\mathrm{T}}\mathbf{X}_{M})^{-1}\mathbf{x}_{i}}], \quad \text{if } i \notin M.$$

(2)

In particular, d_i for $i \notin M$ is the scaled prediction error relative to the subset M. Because d_i follows a Student t distribution, outliers in Y are tested with the statistics $t_{\alpha/2(i+1),i-k}$, where $\alpha/\lceil 2(i+1) \rceil$ is the probability level and (i + k) is the degree of freedom. For given data sorted in order of increasing magnitudes, all observations where $d_i \ge t_{x/2(i+1),i-k}$ are considered outliers.

The overall Hadi and Simonoff method is based on a forward search algorithm consisting of two steps:

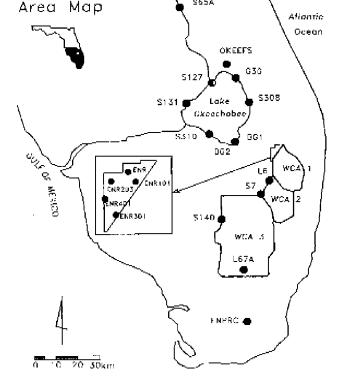
- (1)Find an initial clean subset M of size h = (n + k - 1)/2. That is, for j = k + 1, ..., h, fit a regression model to the subset B of size j_i compute $d_i (i = 1, ..., n)$: arrange $x_i (i = 1, ..., n)$ in ascending order of d_{1} .
- (2)For j = h + 1, ..., n, fit a regression to the subset B of size j; compute $d_i(i = h + 1, ..., n)$ by Eq. (2): arrange $x_i (i = h + 1, ..., n)$ in ascending order of d_{ij} if $d_t \ge t_{x/2(t+1),t-k}$, declare all observations satisfying this condition as outliers and stop the computation, or otherwise, form a new subset of size i + 1by taking the ordered x_{j+1} until j + 1 - n.

In this approach, the significance level α is the only constant (lurning point) to input prior to analysis.

2. Materials and methods

2.1. Data collection

The District initiated its atmospheric deposition monitoring program in 1974 by installing four bulk (both wet and dry) rainfall samplers near Lake Okeechobee and WCA I areas. The monitoring program was significantly improved in 1987 by deploying wet/dry collectors (Acrochem Metrics Model 301 automatic wet/dry samplors) and adopting a standard operating procedure for data collection and processing in accordance with recommendations of the National Atmospheric Deposition Program (Bigelow and Dossett, 1988; NADP, 1996).



\$65A

Fig. 1. Location map showing the atmospheric deposition monitoring sites operated by the South Florida Water Management District, where WCA stands for water conservation area.

Currently, there are 18 monitoring sites with one replicate sampling site (BG2) operated by the District (Fig. 1) from which wet and dry samples are collected separately to estimate atmospheric deposition rates, particularly for nutrients. This study selected the data collected from 7 April 1992 to 22 October 1996, but the actual record lengths vary from site to site owing to periodic expansion of the monitoring program (Table 1).

The Aerochem wet/dry collectors were placed on 1 m high tables at each site. A movable lid operated by a moisture sensor plate was designed so that the lid moves over and covers the dry bucket when it is raining, and covers the wet bucket when it is not raining, to prevent evaporation. The Aerochem bucket opening had an area of 0.0647 m^2 and a height of 0.25 m. Both wet and dry deposition samples were collected at weekly time intervals.

To sample dry deposition, the sample bucket was inspected in the field for contamination and some sources of contamination (e.g. insect and insect parts, amphibians, and reptiles) were removed by hand using tweezers. Any visible contamination was identified according to 39 possible contamination sources. Then, 11 of deionized water was added to rinse the sides of the bucket. The bucket was rubbed with a precleaned plastic spatula. Each water sample was placed into multiple Table 1

Frequency table of visually observed contaminated and uncontaminated dry deposition samples taken from the District's Rainfall Sampling Network from 6 April 1991 to 22 October 1996

Station	Date of first collected sample	No contamination		Single contamination		Multiple contaminations		Total number of samples
		Number	Percent	Number	Percent	Number	Percent	
BG1	09/07/93	85	55.9	14	9.2	53	34.9	152
BG2	09/07/93	88	57.9	12	7.9	52	34.2	152
ENPRC	11/17/87	27	20.6	47	35.9	57	43.5	131
ENR101 ^a	03/22/94	0	0.0	20	24.4	62	75.6	82
ENR203*	01/11/94	0	0.0	18	21.4	66	78.6	84
BNR301*	03/22/94	0	0.0	27	26.2	76	73.8	103
3 NR401 *	12/07/93	0	0.0	x	18,2	36	81.8	44
ENR	03/31/92	11	4.7	61	26.1	162	69,2	234
G36ª	09/07/93	0	0.0	9	22.5	31	77.5	40
L67A	11/21/95	11	29.7	16	43.2	10	27.0	37
L6	11/16/95	3	7.5	19	47.5	18	45.0	40
OKEEFS	11/24/87	47	25.8	44	24.2	91	50.0	182
\$127*	09/07/93	0	0.0	16	24.2	50	75.B	66
\$131	09/07/93	102	68.0	12	8,0	36	24.0	150
S140	06/26/89	26	14.5	72	40.2	81	45.3	179
\$308"	08/09/94	0	0.0	0	0.0	13	100.0	13
\$310	09/07/93	93	67.9	5	3.6	39	28.5	137
S65A°	09/25/89	0	0.0	33	21.6	120	78,4	153
S7	12/05/88	18	8.2	85	38.6	117	53.2	220
Total		511	23.6	518	23.2	1170	53.2	2199

"Data from these stations are dropped for further analysis.

175 ml bottles and acidified with a 50% reagent-grade solution of H_2SO_4 to a pH less than 2. The bottles were stored on ice and returned to the District laboratory within a few hours. At the laboratory, samples were digested with persulfate and P concentration was determined colorimetrically (USEPA, 1979). Quality assurance and quality control were performed in accordance with District standards (SFWMD, 1996). The P deposition (PDEP) rate (µg P m⁻² d⁻¹) was then determined as

$$PDEP = \frac{\lfloor P \rfloor V}{0.0647d},$$
(3)

where [P] is the P concentration in the sample ($\mu g l^{-1}$), V is the volume of water collected (l), 0.0647 is the area of the bucket (m^2), and *d* is the number of days the bucket was deployed.

2.2. Oullier detection

A preliminary step in removing outliers involved screening the samples using descriptions provided in field notes, especially those samples with visual descriptions of gross contamination. These samples were flagged and if their P values exceeded two standard deviations from the mean of all samples, they were discarded. This provided a binary decision of whether each sample was contaminated for a given contamination category. Additional screening was performed using the Hadi and Simonoff approach, described below, to detect outliers and to remove samples contaminated by sources that were not flagged by visible inspection.

To identify the outliers in a data set Y from a given site, the P data from nearby sites were used to determine a independent (explanatory) variable X. Before applying the Hadi and Simonoff approach, the dependent variable $\{y_{i}, i = 1, ..., N\}$ for each site was divided into two subsets: a complete data set $Y_{C} = y_{i}, i = 1, ..., N_{C}$ for which the corresponding explanatory variable x_{i} is available, or an incomplete data set $Y_{1} = y_{i}, i = 1, ..., N_{1}$ for which x_{i} is missing, where $N(=N_{C} + N_{1})$ is the sample size of Y. Then, a linear regression model of

$$y_i = a + bx_i \quad \text{for } i = 1, \dots, N_C \tag{4}$$

was applied to the complete data set where a and b are the regression parameters. Due to the large number of

	2
	Ē
\sim	Frequency
ų.	Ē
-9-	- È
Ē	ļΞ

Frequency table of visually observed contaminations in 1688 dry deposition samples taken from the District's Rainfall Sampling Network from 6 April 1991 to 22 October 1996

'n

ş

Site	Animal droppings and frogs	oppings	Dirt and dust	lust	Vegelation	_	unsects, insect body parts and reptiles	sect body reptiles	TISE:		Misoclianeous	sous	[ota]
	Number	Percent	Number	Percent	Number	Percent	Number	Percent	Number	Percent	Number	Percent	
BGI	5	14.8	46	32.4	9	4.2	33	23.2	8	19.7	~	5.6	142
BC2	13	15.9	87	34.8	φ	6.5	52	18.1	5	19.6	г-	5	138
ENPRC	6 7	29.9	5	34,8	-1	55	36	22.0	Ι	0.6	Or.	55	164
ENRIOI	5	19.0	57	32.8	[~	$^{4.0}$	58	13.J	Π	6.3	20	4.6	174
ENR203	Ŕ	22.8	5 25	32.2	¢	0.0	60	35.1	14	8,2	n,	1.8	171
ENR301	84	24.9	71	36.8	r)	1:0	55	30.1	9 0	4.1	÷	3.1	191
ENR401	56	28.0	25	26.9	1	1.1	30	32.3	(7.5 2	त्त	43	5
ENR	46	10.6	162 1	37.3	15	3.5	130	30.0	寺	1.01	ž	8.5	454
G36	30	36.6	25	30.5	٥	0.0	18	22.0	~	6.1	σ	4.9	82
L67A	ন	10.8	15	40.5	0	0.0	12	32,4	0	0.0	9	16.2	37
Lá	ম	6.6	18	29.5	-	1.6	27	4 .3	¢	9.8	v)	N %	19
OKEEFS	£	[5.7	011	4.4 4	-	10 10 10	5	20.6	ম	<u>, 1</u>	53	6.6	248
51 27	52	38.0	35	25.5	v,	3.6	33	24.1	না	65	90	5.8	137
5131	16	15.8	엄	31.7	9	5.9	ጽ	29.7	¢	6.9	90	6.1	101
S140	8	21,7	5	37.8	30	3.2	[~ 寸	18.9	<u>n</u>	5.2	18	22	249
S308	잌	36.4	ō	27.3	0	0.0	5	21.2	2	6.1	÷	9.1	Υ.
S310	~	4.F	33	5 1 1 1	ر ی	3.2	37	38.9	1	12.6	.	3.2	<u>9</u> 5
S65A	112	36.5	<u>9</u> 3	30.3	ი	2.9	57	18.6	~	2.6	78	9.1	307
5	읽	5.9	164	47.7	÷	I .2	82	23.8	36	10.5	36	7.6	344
Total	199	20.6	1149	35.9	601	3.4 2.5	831	25.9	239	5.5	214	6.7	3203
Percent		30.1		52.3		5.0		37.8		6.01		6.6	145.7

missing data that occurred randomly, $N_{\rm C}$ was commonly less than N. To increase $N_{\rm C}$, 1–4 explanatory sites were chosen based on the distance between sites, periods of record, and the number of missing data. An average of the P values measured concurrently from the selceted explanatory sites was then taken as an independent variable.

3. Results

The 39 distinct contamination sources were assigned one of six categories (animal droppings and frogs, dirt and dust, vegetation, insects and reptiles, ash, and miscellaneous) (Table 2). Only 511 of the 2199 samples showed no visible signs of contamination (Table 1). These 511 samples were found at 11 of the 19 stations. Multiple contaminations of samples were very common. A total of 518 cases of single and 1170 multiple contamination cases were recorded.

Because of multiple contaminations there were 3203 observed sample contaminations in the 2199 samples (Table 2). Of the total observed contaminations, the most common were dirt and dust which comprised 35.9% of observations and were found in 52.3% of all samples. This was followed by insects and insect body parts (25.9% of observations, 37.8% of samples), and animal droppings (20.6% of observations and 30.1% of samples). Ash, miscellancous, and vegetation made up less than 18% of the observations and were found in less than 26% of the samples.

Preliminary inspection of the uncensored P data showed a number of high values (for instance, Prob. $\{P > 1000 \ \mu g \ P \ m^{-2} \ d^{-1}\} \approx 4\%$, Fig. 2) that were assumed to be contaminated since natural deposition processes are unlikely to yield such high concentrations. Summary statistics of P deposition then were computed for each contamination category (data not shown). No relationships between P and contamination category could be detected because of high variability of contamination and multiple contamination sources in a sample. Consequently, salvaging the contaminated data by separating the true atmospheric deposition component and contamination component was not possible.

Animal droppings and frogs were the most significant contamination source: the mean P value was $4486 \pm$ 15 010 µg P m⁻² d⁻¹. Contributions from the other catcgories were relatively small. Samples that were contaminated by animal droppings and frogs with the P value greater than 884μ g P m⁻² d⁻¹ (a value two standard deviations from the mean of uncensored P data) were therefore eliminated from further analysis (Table 3). Based on this first step, 2.3% of the data were eliminated. Although most of the high P deposition data were effectively removed using this approach, there were still unreasonably high P values remaining.

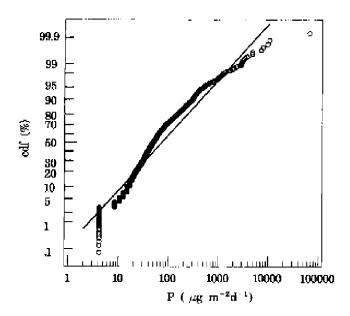


Fig. 2. Frequency distributions of raw dry deposition P data (2199 data points) from 19 monitoring sites before removing nutliers, with the best fitted linear regression line. Note: The data less than the method detection limit (MDL) of 8.8 μ g P m⁻² d⁻¹ were assigned a value of MDL/2 for plotting purpose.

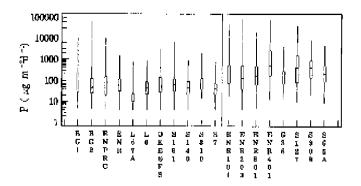


Fig. 3. Box and whisker plots of dry deposition P values from 19 sites in South Flotida. The solid line represents the mean at each site, while the middle, bottom and top edges of each hox are the median, 25th and 75th percentiles, and the bottom and top of whiskers are the low and high extremes, respectively.

Of the 19 sites, only 11 sites were analyzed further because the data from the other eight sites (Table 1) had high rates of contamination (Fig. 3) resulting in failure of the Hadi and Simonoff approach due to unusually low computed d_i values. For each site, the Hadi and Simonoff approach was applied to the complete data set, from which outliers and a site-specific cutoff value were determined based on the *t*-statistics $f_{\alpha/2(l+1),l-k}$. The site-specific cutoff value was then used to identify the outliers in an incomplete data set Y_1 .

Fig. 4. Examples of outlier detection for the selected sites, where outliers are the right-hand-side data points (*) along the vertical reference (cutoff) line which represents the z-value for $\alpha = 0.01$.

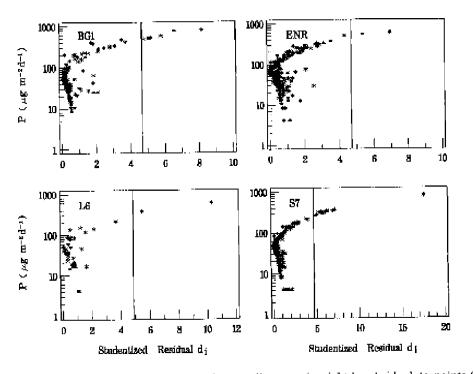
To assess the performance of the Hadi and Simonoff approach, the estimated d_i versus P value was plotted for four arbitrarily selected sites (although all sites showed nearly identical patterns) (Fig. 4). Since the data in each plot are for the complete data set having a size of N_c , the number of outliers displayed in each plot is less than the corresponding number for the total number of samples N (Table 3). For instance, at site BG1, only six outliers

Table 3	
Summary of outlier detection for 1614 dry P c	leposition samples from 11 stations

Station name	Number of detected outliers		Number of samples after removing	Outlier bound (ug P m ^{- 2} d ⁻¹)	Mean $(\mu g P m^{-2} d^{-1})$	Standard deviation $(\mu g \mathbf{P} \mathbf{m}^{+2} \mathbf{d}^{-1})$
	Field notes*	Statistical approach	outliers			
н	6	22	124	> 435	85.6	91.9
BG2	7	18	127	> 232	79.7	89.1
ENPRC	5	32	94	> 627	69.3	86.0
ENR	3	15	216	> 386	89.3	82.6
L67A	0	8	29	> 46	17.8	11.4
L6	Ő	7	33	> 230	60.6	51.8
OKREFS	10	34	138	> 488	85.5	87.4
S131	5	26	119	> 499	91.1	82.0
5140	1	36	142	> 307	74.5	77.9
\$310	ō	25	112	> 355	92.1	77.4
S7	ò	31	189	> 241	77.3	88.4
Sum	37	254	1443			
• •	(2.3%)	(15.7%)	(82.0%)			
Mean	· · ·	· •		> 350	74.8	75.1
	tistical outlier dete	ction			85.8	79.0

II. Ahn, R.T. James / Atmospheric Environment 33 (1999) 5123-5131

*Includes samples contaminated with bird droppings or frogs if P value $>884~\mu g$ P m $^{-2}$ d $^{-1}.$



are displayed but there are 22 detected outliers if we consider both the Y_1 and Y_0 data sets. The results of our outlier detection are not sensitive to the choice of significance level α . This insensitivity is attributed to the significantly large values of outliers compared to the non-contaminated samples. Because of these distinct differences, the results of outlier detection were consistent regardless of the sample size and the number of detected outliers (although the R^2 in regression was very low in most cases; $R^2 = 0.3-0.7$). In other words, the goodness-of-the-fit of a regression is not critical for outlier detection.

The cutoff values for determining outliers varied from site to site depending on the occurrence of data contamination (column 5 in Table 3). An average of the distributed cutoff values from the 11 stations was $350 \ \mu\text{g} \ \text{Pm}^{-2} \ \text{d}^{-1}$. However, this value was less reliable because it was affected by the distribution of an outlying data set. The computed means for each station ranged from 17.8 $\ \mu\text{g} \ \text{Pm}^{-2} \ \text{d}^{-1}$ at L67A to 92.1 $\ \mu\text{g} \ \text{Pm}^{-2} \ \text{d}^{-1}$ at S310. The sample mean of dry P deposition from the 11 stations was 74.5 + 75.5 $\ \mu\text{g} \ \text{Pm}^{-2} \ \text{d}^{-1}$.

4. Discussion

An accurate account of P loads is needed to understand its impact on the Everglades. This account must include surface loads, rainfall, and dry deposition. The latter is significant, however, contamination from bird droppings, body parts of insects, and miscellaneous debris, as documented here, is problematic in obtaining accurate background rates of dry P deposition. This problem is not an isolated one, and extends to almost all projects that measure atmospheric deposition. The method employed here is useful and defensible in removing the bias of contamination for multi-site data.

Estimates of P dry deposition range from 4 to 10 times that of wet deposition (Hicks et al., 1993). Wet deposition in South Florida, with a mean rainfall of 1.35 m yr⁻¹ and a mean concentration of 10.6 μ g P I⁻¹ (Abn, 1998) in rainfall, is estimated as 14.3 mg P m⁻² yr⁻¹. Our observed estimate of dry deposition is 27.3 mg P m⁻² yr⁻¹ (calculated from Table 3). Thus, the ratio of our dry deposition to wet deposition is 2 : 1, which is lower than what others have observed.

The total estimate of wet deposition plus dry deposition, 41.6 mg P m⁻² yr⁻¹, is consistent with estimates from peat accretion data of 35.5 mg P m⁻² yr⁻¹ (Walker, 1993), and 50 mg P m⁻² yr⁻¹ from bulk collectors throughout Florida (Hendry et al., 1981). But it is less than the 93.3 mg P m⁻² yr⁻¹ determined in the Tampa area from seven bulk collectors (Dixon et al., 1996). These comparisons provide a certain level of confidence regarding the District's sampling network, procedures, and the statistical approach that we have taken. However, there is still a large amount of variability within our own data. Dry deposition is quite variable both in space (11)cks et al., 1993; Van Ek and Draaijers, 1994; Dixon et al., 1996; Hendry et al., 1981), and time (11)cks et al., 1993). The latter is primarily a result of episodic events and deposition of larger (>2 μ m) particles. Both the spatial and temporal variability are also present in the data from the District's network of atmospheric deposition stations. The standard deviation of the samples is equivalent to the mean (after censoring). Also the means ranged from an average of 17.8 μ g P m⁻² d⁻¹ at a remote station in a marsh area of the Everglades (1.67A) to 92.1 μ g P m⁻² d⁻¹ at S310 a site near the town of Clewiston that is impacted by industrial activity.

As a result of data screening based on the two-step procedure, about 18% of the data were identified as contaminated and were removed. The pooled mean and standard deviation of the dry P data collected from 11 sites was 74.8 \pm 75.1 μg P m $^{-2}$ d $^{-1},$ and is actually lower than other estimates of dry deposition in the state of Florida. Dixon et al. (1996) estimated $120.5~\mu g$ P m $^{-2}$ d $^{-1}$ from the Tampa area, Hendry et al. (1981) estimated 131 μ g P m⁻² d⁻¹ from four sites in one orban, two agricultural, and one sea side area, and Peters and Reese (1995) measured 194 μ g P m⁺² d⁻¹ south of Lake Okecchobee in May-June of 1992. Our lower estimates are most likely a combination of improved field observations, sampling methods, and location of the samplers in areas that are further away from urban centers, industry (such as the phosphate mining industry in the Tampa area), and traffic.

A major question regarding dry deposition is how much is from external or background atmospheric deposition, and how much is from internal or local sources. This question not only deals with the problem of contamination but also methods of collecting dry deposition. Because of the relative simplicity and robustness of this outlier identification technique, it should be useful for any dry deposition collection method.

5. Summary

This study took an observational and statistical approach to detect outliers in the dry deposition P samples. The approach used both field notes describing the type of contamination and outlier detection statistics based on a linear regression. In particular, the study demonstrated how a two-phased outlier detection approach can be applied for multi-site environmental data. Although this approach cannot remove all uncertainty from these data, it did produce a pooled value of 74.8 μ g P m⁻² d⁻¹ that was 10% less than the pooled value of prescreened data of 85.8 μ g P m⁻² d⁻¹. The forward search algorithm proposed by Hadi and Simonoff (1993) for finding a clean subset was fast and robust as was reported in the

previous studies. This approach was not sensitive to the significance level which is the only turning point in the outlier detection method. This method should be useful to other studies for screening dry deposition samples.

Acknowledgements

The authors are grateful to Cheol Mo and Maria Loucraft-Manzano for discussions early in the work, and to Todd Tisdale, Zhen Chen, Mike Chimney, and two anonymous reviewers for constructive comments on the manuscript.

References

- Ahn, H., 1998. Outlier detection in total phosphorus concentration data from South Florida rainfall, Technical Publication. WRE-351, South Florida Water Management District, West Palm Beach, FL, 35pp.
- Atkinson, A.C., 1994. Fast very robust methods for the detection of multiple outliers. Journal of the American Statistical Association 89, 1329-1339.
- Burnett, V., Lewis, T., 1984. Outliers in Statistical Data. second ed. John Wiley, New York.
- Beckman, R.J., Cook, R.D., 1983. Outliers.....s. Technometries 25 (2), 119-149.
- Bigelow, D.S., Dossett, S.R., 1988. NADP/NTN Instruction Manual: Site Operation, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, 114pp.
- Davis, S.M., 1994. Phosphorus inputs and vegetation sensitivity in the Everglades. In: Davis, S.M., Ogden, J.C. (Eds.), Everglades – the Ecosystem and Its Restoration. St. Lucie Press, St. Lucie, FL, pp. 357–378.
- Dixon, L.K., Murray, S., Perry, J.S., Minotti, P.J., Henry, M.S., Pierce, R.H., 1996. Assessment of bulk atmospheric deposition to the Tampa Bay Watershed. Final Report submitted to the Tampa Bay National Estuary Program, St. Petersburg, FL.
- Erisman, J.W., Beier, C., Draaijers, G., Lindgerg, S., 1994. Review of deposition monitoring methods. Tellus 46B, 79-93.
- Graham, W.F., Duce, R.A., 1982. The atmospheric transport of phosphorus to the western North Atlantic. Atmospheric Environment 16, 1089-1097.
- Hadi, A.S., Simonoff, J.S., 1993. Procedures for the identification of multiple outliers in linear models. Journal of the American Statistical Association 88, 1264–1272.
- Hadi, A.S., Son, M.S., 1990. Some properties of and relationships among, several uncorrelated and homoscodastic resid-

ual vectors. Communications in Statistics. Part A – Theory and Methods 19, 2625-2642.

- Hawkins, D.M., Simonoff, J.S., 1993. High breakdown regression and multivariate estimation. Applied Statistics 42, 423-432.
- Hendry, C.D., Brezonik, P.L., Edgerton, E.S., 1981. Atmospheric deposition of nitrogen and phosphorus in Florida. In: Eisenreich, S.J. (Ed.), Atmospheric Pollutants in Natural Waters. Ann Arbor Sci., Publ, Ann Arbor, MJ, pp. 199-215.
- Hicks, B.B., 1986. Measuring dry deposition: a re-assessment of the state of the art. Water, Air and Soil pollution 30, 75-90.
- Hicks, B., McMillan, R., Turner, R.S., Holdren Jr., G.R., Strickland, T.C., 1993. A national critical loads framework for atmospheric deposition effects assessment: III. Deposition Characterization. Environmental Management 17, 343-353.
- Lawson, D.R., Winchester, J.W., 1979. Sulfur, potassium and phosphorus associations in acrosols from South American tropical rain forests. Journal of Geophysical Research 84, 3723-3727.
- NADP, 1996, NADP/NTN Wet deposition in the United States 1995, National Atmospheric Deposition program, Colorado State University, Fort Collins, CO, 11pp.
- Peters, N.E., Reese, R.S., 1995. Variations of weekly atmospheric deposition for multiple collectors at a site on the shore of Lake Okeechobee. Florida. Atmospheric Environment 29, 179–187.
- Redfield, G.W., 1998. Quantifying atmospheric deposition of phosphorus: a conceptual model and literature review for environmental management. Technical publication WRE #360. South Florida Water Management District, West Palm Beach, FL, 35pp.
- Rousseeuw, P.J., Van Zomeren, B.C., 1990. Unmasking multivariate outliers and leverage points (with discussion). Journal of the American Statistical Association 85, 633-651.
- SFWMD, 1996. SFWMD comprehensive quality assurance plan. WRF-346, South Florida Water Management District, West Palm Beach, FL.
- State of Florida, 1994. Everglades Forever Act Chapter 373,4891. Florida Statutes, Tallahassee, FL.
- Tiwari, R.C., Dienes, T.P., 1994. The Kalman filter model and Bayesian outlier detection for time series analysis of BOD data. Ecological Modelling 73, 159-165.
- USEPA, 1979. Methods for Chemical Analysis of Water and Wastes. United States Environmental Protection Agency, Washington, DC.
- Van Ek, R., Draaijers, G.P.J., 1994. Estimates of atmospheric deposition and canopy exchange from three common tree species in the Netherlands. Water, Air, and Soil Pollution 73, 61-82.
- Walker, W.W., 1993. A mass-balance model for estimating phosphorus settling rate in Everglades Water Conservation Area 2A. Prepared for the U.S. Department of Justice, 20pp.

.

.

ł

ē

¥.

í.