

Assessment of nitrogen and phosphorus loading by atmospheric dry deposition to the Lagos Lagoon, Nigeria

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Abstract Surface water pollution has been found to be considerably driven by the contributions of airborne particles, open-air waste burning and fossil fuel combustion, ammonia volatilization from excreta, fertilizer and derivatives from explosive factories. Atmospheric deposition into the Lagos Lagoon is suspected to be a major contributor to the nutrient levels of the lagoon. Atmospheric dry nutrient deposition was monitored at six stations around the Lagos Lagoon from January to June 2012 in order to estimate the contribution of atmospheric deposits into the lagoon's nutrient cycles. Species of phosphorus (P) and nitrogen (N) in the lagoon water were analyzed by colorimetric methods. Mean $[\text{NO}_3^- + \text{NO}_2^-]$ -N was $3.08 \pm 2.10 \text{ mg m}^{-2} \text{ day}^{-1}$ ($0.55\text{--}8.73 \text{ mg m}^{-2} \text{ day}^{-1}$). The $(\text{NO}_3^- + \text{NO}_2^-)$ -N was only about 2 % of total N but $[\text{NH}_4^+ + \text{organic}]$ -N was approximately 38 % of total N. Particulate N was about 60 % of total N. Average total N was $144 \pm 94.9 \text{ mg m}^{-2} \text{ day}^{-1}$ ($48.0\text{--}285 \text{ mg m}^{-2} \text{ day}^{-1}$). Average soluble reactive P was significantly lower than $[\text{NO}_3^- + \text{NO}_2^-]$ -N averaging about $0.12 \pm 0.12 \text{ mg m}^{-2} \text{ day}^{-1}$. Soluble reactive P (SRP) was less than 2 % of total P but soluble organic P was about 86 % of total P. Particulate P accounted for about 12 % of total P. Average total P was $4.56 \pm 10.1 \text{ mg m}^{-2} \text{ day}^{-1}$ ($0.48\text{--}31.6 \text{ mg m}^{-2} \text{ day}^{-1}$). This study shows that atmospheric deposition of nutrients into the Lagos Lagoon is

taking place and this may represent a considerable proportion of the total nutrient loading of the lagoon.

Keywords Dry deposition · Surface-water pollution · Nitrogen · Phosphorus

Introduction

Sustained urbanization and industrialization with attendant increases in on-road vehicles have markedly disturbed the natural atmospheric balance of major and rapidly expanding cities. These anthropogenic environmental pressures diminish air quality around these cities through the introduction of particulates, NO_x and SO_x gases, and other airborne pollutants into the atmosphere. Though, the air quality of an area has to be considered in a wider context because tropospheric chemistry also includes gases released by natural sources such as volcanic activities and biomass decomposition (Monks et al. 2009), nevertheless, anthropogenic contributions have steadily been increasing over the years in spite of stringent regulatory checks by various countries to keep the levels tolerable.

While direct inputs from anthropogenic sources steadily build up over a localized area, carry-over from a proximate urban centre can also be moved to another city by advection thereby leading to regional air pollution problems covering an expansive area (Boubel et al. 1994). Once emitted into the atmosphere, gaseous nitrogen compounds for example, may be deposited locally or borne over great distances before being

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deposited (Celle-Jeanton et al. 2009). During these often long transport periods, slow-reacting primary air pollutants such as NH_3 , NO and SO_2 , emitted from diverse sources, undergo various reactions to form NO_2 and SO_3 which in turn react with atmospheric water vapor to produce their corresponding acids (Schindler et al. 1996; Aneja et al. 2006). These acids react with numerous compounds to give nitrates and sulphates which occur as sub-micrometre particulates (Erisman et al. 2007; Santachiara et al. 2012).

Particulates and pollutant gases could be deposited on surfaces and scavenged from the atmosphere through two principal pathways, namely precipitation (wet deposition) and gravitational settling (dry deposition) (Erisman et al. 2005). In the former mechanism, the particles act as additional condensation nuclei in cloud formation and are deposited if the droplets grow to sufficient size to fall as raindrops and/or the particles can also be captured by raindrops falling through the air (Santachiara et al. 2012). In the latter pathway, the particles come in contact with and stick to surfaces of water bodies, vegetation, soil and buildings due to gravitational pull.

Open burning of anthropogenic and biogenic materials is rampant in developing nations including Nigeria and serves as a constant source of particulates of nitrates, phosphates and sulfates (Boubel et al. 1994). For example, as deforestation and agricultural activities increase, the amount of dry atmospheric deposition will likely increase (Ramlal et al. 2003) with atmospheric input mostly accounting for a significant proportion of the nutrient flux to aquatic and terrestrial ecosystems (Morales et al. 2001; Schindler 2009). Besides the primary consequence of eutrophication and acidification of ecosystems by dry and wet atmospheric deposition of gases and aerosols, particulate nitrates and sulfates arising from secondary particle formation can also impair visibility (Erisman et al. 2005).

In the N cycle, N_2O and NO_x are the least thermodynamically stable forms. These and atmospheric NH_3 are deposited onto the soils and waters. Also, atmospheric N_2 is fixed into the soil as NH_3 by *Rhizobium* (associating with leguminous plants) and into waters by photosynthetic bacteria, *Azotobacter*, *Cyanobacteria* and *Clostridium* (Harrison, 2007). Atmospheric N_2 could also be converted to fertilizer in NH_4^+ and NO_3^- forms. Water bodies also receive N from fertilizer runoff and sewage (Schindler et al. 2006). In aerobic soils and aquatic systems, reduced N forms (NH_x) are oxidized by micro-organisms to NO_2^- and further to NO_3^- . The

latter is assimilated by plants and some micro-organisms to synthesize amino acids and proteins, which are the most thermodynamically stable forms of N. The death of plants and animals returns organic N to terrestrial and aquatic systems where microbiological decomposition converts organic N to NH_4^+ , which can undergo further oxidation to NO_3^- or be directly assimilated by plants. Reduction of NO_3^- to N_2 returns N back to the atmosphere (Geurts et al. 2010).

In the P cycle, orthophosphate is converted to organic P after plant uptake from soil and waters. Animals including fish ingest organic P from plants and return it to soil and waters via excretion. The animal excreta from soil can be washed into waters and a portion of the P will settle in the sediment. P fertilizer runoff as well as weathering and erosion of phosphate rocks also deliver P to water bodies. Decomposition of excreta as well as dead plants and animals convert organic P to orthophosphate in soil and waters while movement of marine sediment to land returns P back to soil (Manahan 2000).

The terrestrial ecosystem incorporates the wet and dry-deposited nitrogen and phosphorus species as nutrient sources whenever possible. Between 30 and 60 % of the nitrogen deposited on land is thought to be absorbed by the ecosystem (Ritter et al. 2002). The degree to which a watershed can retain nutrients is a function of the soil characteristics, topography, underlying geology, the amount and type of surface vegetation and the degree of impervious cover. Inevitably, a significant amount of deposited nutrient will be transported during a precipitation event, via overland or subsurface flow, into a freshwater system. Usually freshwater systems are phosphorus-limited and may not use the available excess nitrogen (Paerl et al. 2004). Thus, most of the nitrogen will be delivered to estuarine systems. Studies have indicated that atmospheric nitrogen accounts for a large portion of the allochthonous nitrogen in estuaries and coastal oceans. For example, North Carolina estuaries may receive between 30 and 40 % of the outside nitrogen from the atmosphere, while coastal oceans may receive up to 50 % from the atmosphere (Ritter et al. 2002).

An important surface water in Nigeria which may be receiving atmospheric deposition of nutrients is the Lagos Lagoon. The Lagos Lagoon and its tributaries are not only a habitat for a diverse flora and fauna species with rich biodiversity but also serves as a source of fishing, water resources for aquaculture and water transportation to the teeming population of Lagos (Babatunde, 2010). The lagoon, the largest of numerous

lagoons along the West African coast, is a shallow brackish coastal lagoon located in Lagos State (3577 km² in size) on the western part of Nigeria within latitude N 06° 26' and longitude E 003° 23' (Adewolu et al. 2009). Over the years, there has been a progressive nutrient enrichment of the lagoon (Abayomi et al. 2011; Alo et al. 2014) with attendant consequences such as eutrophication, hypoxia (Alo et al. 2010) as well as a general deterioration of the water quality and esthetics of the lagoon. These have negatively impacted on the economic fortunes of its dependants and the city in general. Therefore, this study aims to determine the quality and quantity of dry deposition inputs into the Lagos Lagoon's nutrient biogeochemical cycles in order to effectively isolate the sources of the inputs for possible remediation effort.

Methodology

Study area

The study was conducted in and around the Lagos Lagoon using six sampling sites (S1 to S6). The sampling sites were located in areas with different land use characteristics as shown in Table 1. Sites S1, S2, S3 and S5 were situated within the Lagos metropolis while sites S4 and S6 were situated on the Lagos Lagoon shoreline (Fig. 1) to capture representatives of the dry nutrients deposited directly into the lagoon. Site S4 was located in a remote part of the lagoon farther from local terrestrial influences than the other locations, ca.150 m from residential buildings and trees and ca.730 m from the major road. This is in contrast to other sampling locations situated within the metropolis. Thus, site S4 was designated as the control site for the study.

Sampling

Dry deposition samples were collected in duplicates into open polyethylene bowls (measuring 0.056 m² in surface area and 0.27 m in height) placed on specially constructed sampling platforms at each site. The sampling platform had a height of 1.0 m from the ground level (Bootsma et al. 1999) to eliminate terrestrial influences. The bowls were each filled with 1 L of distilled and deionized water before being placed on the platform and thereafter exposed for 24 h after which they were retrieved. On retrieval, the deposit samples were

Table 1 Description and attributes of sampling sites

Sampling site	Site description	Site attributes
S1	16 km away from the lagoon and within the metropolis	Densely populated, high traffic, high commercial business powered by generating sets
S2	12 km away from the lagoon and within the metropolis	Densely populated, high traffic, highly industrialized, high commercial business powered by generating sets
S3	7 km away from the lagoon and within the metropolis	Densely populated, high traffic, highly industrialized, high commercial business powered by generating sets
S4	Shoreline, about 730 m from the road linking it to the metropolis	Sparsely populated with scattered buildings
S5	3 km away from the lagoon and within the metropolis	Densely populated, high traffic, high commercial business powered by generating sets
S6	Shoreline, about 160 m from the road linking it to the metropolis	Densely populated, high traffic, high commercial business powered by generating sets

transferred into 1.5 L polyethylene bottles which had been pre-washed with 5 % HCl (v/v) solution and adequately rinsed with deionized water. A total number of 36 samples were collected sampling locations used for the study.

Sample preservation and quality control

All plastic and glass artefacts used in the study were soaked in 5 % HCl (v/v) for 48 h and adequately rinsed with distilled and deionized water in the laboratory. They were then dried and packed in transparent polyethylene bags before being used. The polyethylene bottles were rinsed with portions of the deposit samples on site before the samples were retained in them. One millilitre of 2.25 M H₂SO₄ (Sigma-Aldrich) was added to every 125 mL sample for total nitrogen and total phosphorus determination to bring its pH below 2.00

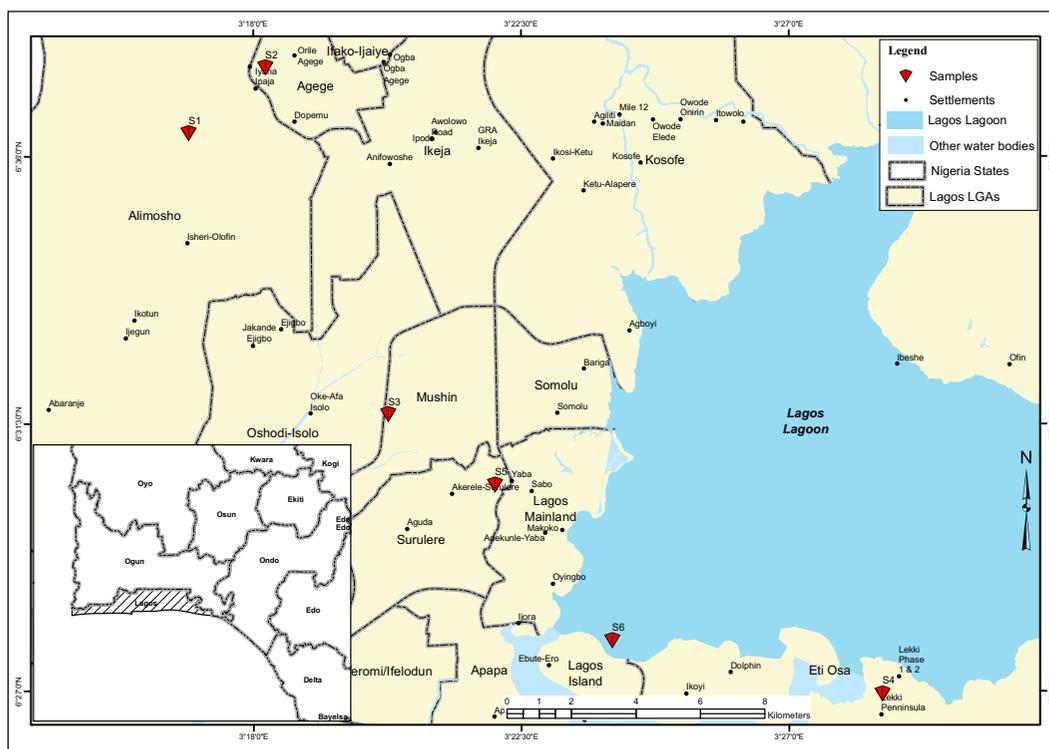


Fig. 1 Map of the study locations

(APHA 2005). Samples retrieved from site were immediately transported to the laboratory and refrigerated at 4 °C. Determination of nitrate and orthophosphate in the samples were carried out within 24 h of sample retrieval. Analytical-grade reagents were used for the analysis of the samples.

Experimental

The pH of the deposit samples were determined by electrometric method using a pH metre (Mettler Toledo AG 8603). The pH metre was calibrated with standard buffers (Mettler Toledo) of pH 4.01, 7.00 and 9.21.

Phosphorus (P) species were analyzed by the Murphy and Riley (APHA 2005) method. Sulphuric acid solution (2.5 M), 8.4 mM potassium antimonyl tartrate solution (BDH Chemicals, UK), 32.4 mM ammonium molybdate solution (BDH Chemicals, UK) and 99.9 µM ascorbic acid solution (Surechem Products, UK) were added and

thoroughly mixed in tandem to prepare a combined reagent. The sample was filtered through a 0.45-µm membrane filter (Whatman) to remove suspended particulates and one drop of phenolphthalein indicator was added. Sulphuric acid solution (2.5 M) was added in drops to discharge the pink colouration observed in some of the samples from site S1. Eight millilitres of the combined reagent was added to 50 mL of the sample and the absorbance of the sample measured between 10 and 30 min at 880 nm against a deionized water reagent blank on a UV/Visible spectrophotometer (Thermo Spectronic, Genesys 10-S). A calibration curve was generated from ten orthophosphate working standard solutions within the range of 40 to 480 µg L⁻¹.

Species of nitrogen (N) were determined by cadmium reduction using the Griess-Ilosvay method (APHA 2005). The copperized cadmium column (18.5 cm in length) was prepared from 25 g 20-mesh sized Cd granules (Alfa Aesar, UK), 6 M HCl (Sigma-Aldrich, Germany) and 100 mL of 2 % CuSO₄ (Surechem

Products, UK). Column was washed with 200 mL of dilute NH₄Cl-EDTA solution composed of 0.146 M NH₄Cl, 2.76 mM Na₂EDTA and 11.88 mM NH₃. The column was activated with 100 mL of a solution composed of 25 % 1 mg L⁻¹ NO₃⁻-N standard solution and a 75 % NH₄Cl-EDTA solution at a rate of 9 mL min⁻¹. Sample pH levels were adjusted to between 7 and 9. Each sample was filtered through a 0.45-µm membrane filter to remove particulates. To 25 mL sample, 75 mL NH₄Cl-EDTA solution was added, mixed and poured into the column. The sample eluent was collected at a rate of 9 mL min⁻¹. The first 25 mL was discarded and the rest was collected into labeled sample bottles.

Within 10 min after reduction, 2 mL of color reagent made up of 1.46 M phosphoric acid (Sigma-Aldrich, Germany), 58.0 mM sulfanilamide (Alfa Aesar, UK) and 3.90 mM N-(1-naphthyl)–ethylene diamine dihydrochloride (Alfa Aesar, UK) was added to 50 mL of the reduced sample and mixed. The absorbance of the sample was measured at 543 nm against a deionized-water reagent blank on a UV-Visible spectrophotometer (Genesys 10-S, Thermo Spectronic). To obtain a standard curve, nitrate standards solutions in a range of 0.05 to 1.0 mg L⁻¹ NO₃⁻-N were used. Reduction column efficiency was verified monthly by comparison with 1.0 mg L⁻¹ NO₃⁻-N standard and Cu–Cd granules were reactivated when efficiency of reduction fell below 75 %.

Total concentration of the various P and N species were determined by digesting 50 mL of sample with

Table 2 The pH data of the dry deposition samples

Station	Number of samples	Mean ± SD	Minimum	Maximum
S1	7	6.15 ± 2.01	2.80	8.51
S2	7	6.54 ± 1.57	3.40	7.72
S3	7	5.94 ± 0.83	4.90	7.00
S4	7	6.46 ± 1.24	4.40	7.70
S5	4	6.31 ± 0.56	5.70	6.79
S6	4	5.36 ± 0.44	5.04	5.81

potassium persulfate (Sigma-Aldrich, Germany). One millilitre of 30 % sulfuric acid solution and 0.5 g K₂S₂O₈ were added in tandem to each sample. The sample volume was then reduced to about 10 mL by boiling on a hot plate. The resulting mixture was cooled and diluted to 30 mL with deionized water and subsequently adjusted to a neutral pH with NaOH solution. It was then made up to 100 mL with deionized water. The nitrate-N and soluble reactive P (SRP) species were determined directly on 0.45-µm filtered samples. Total dissolved N (TDN) and total soluble P (TSP) were determined on filtered and persulfate-digested samples. The [NH₄⁺+organic]-N species was estimated as the difference between TDN and NO₃⁻-N, and soluble organic P as the difference between TSP and SRP. Total N (TN) and total P (TP) were determined on unfiltered and persulfate-digested samples. Particulate N was estimated as the difference between TN and TDN, and particulate P as the difference between TP and TSP.

Fig. 2 Concentrations of nitrate-N and soluble reactive P

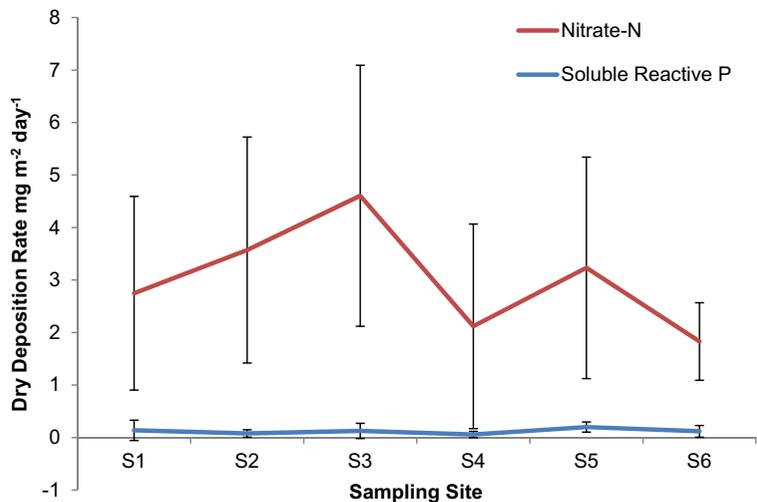
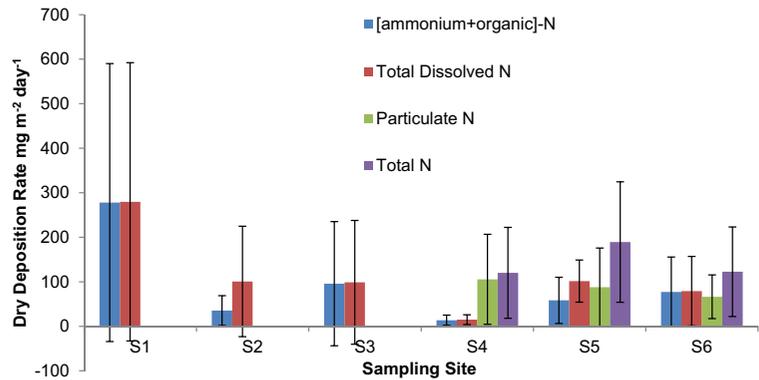


Fig. 3 The dry deposition rates of the nitrogen species at the sites



Results and discussion

The results of the samples' pH measurement are shown in Table 2. The pH values ranged from 5.36 ± 0.44 to 6.54 ± 1.57 . The overall mean pH value of the dry deposition was 6.17. This value is higher than the 5.60 predicted by equilibrium with atmospheric carbon dioxide (Morales et al. 2001).

The results of the N species in the dry deposition samples are illustrated in Figs. 2 and 3. Mean $[\text{NO}_3^- + \text{NO}_2^-]$ -N ranged from 1.70 ± 0.74 to $4.48 \pm 2.48 \text{ mg m}^{-2} \text{ day}^{-1}$ ($n = 36$) (Fig. 2). Particulate N constituted about 60 % of the total N (TN) in the dry deposition samples (Fig. 3). The $[\text{NO}_3^- + \text{NO}_2^-]$ -N species was only about 2 % of the TN. The $(\text{NH}_4^+ + \text{organic})$ -N was about 38 % of the TN. Average TN was $144 \text{ mg m}^{-2} \text{ day}^{-1}$ (48.0 – $285 \text{ mg m}^{-2} \text{ day}^{-1}$). The high quantities of nitrogen species in the deposition sample may have been due to the significant fossil fuel and biomass burning and industrial transportation activities within and around the Lagos metropolis.

Total dissolved N was dominated by $[\text{NH}_4^+ + \text{organic}]$ -N. Hence, the similarity in their deposition trends (Fig. 3). This suggests a considerable deposition rate of

ammonium ions/organic nitrogen. In Figs. 2 and 3, the control site (S4) consistently had the lowest deposition thus the most depressed bars while S1, S3 and S5 had comparative higher deposition rates. The low deposition recorded for S4 was consistent with the fact that it was located farther from local influences compared to other sampling locations. It also had the minimum dispersion or variability in its data as reflected in the error bars of the graphs. This indicates that S4 was fed by atmospheric deposition which may have originated from long-range transport of pollutants whereas other sites were fed by both emissions from their local environment and carry-over emissions from long-range transport of pollutants. The high variability of the observed depositions as shown in Fig. 3 was due to rain events (rainout and washout) which would depress pollutant levels and introduce variation proportionately to the amount of rainfall in addition to the combined influence of erratic local emissions and carry-over emissions from long-distance transport of pollutants.

The results of P in the dry deposition samples are as shown in Figs. 2 and 4. Mean levels of soluble reactive P (SRP) in the samples ranged from 0.06 ± 0.06 to $0.14 \pm 0.19 \text{ mg m}^{-2} \text{ day}^{-1}$ ($n = 36$) (Fig. 2). This was

Fig. 4 The dry deposition rates of the phosphorus species at the sites

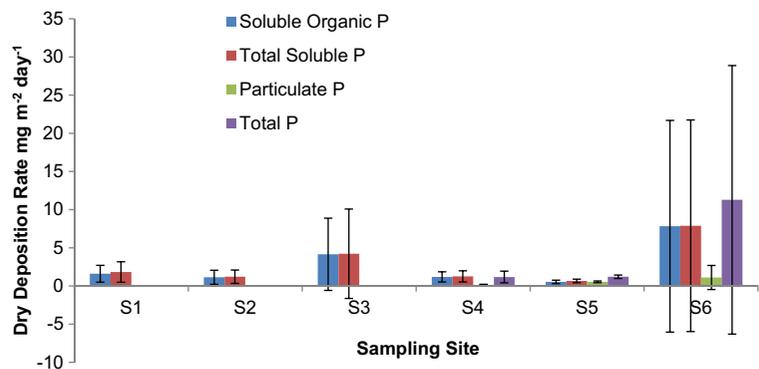


Table 3 Molar mean ratios of total N to total P at three sites

Station	Mean TN (mmol m ⁻² day ⁻¹)	Mean TP (mmol m ⁻² day ⁻¹)	TN:TP
S4	8.58	0.04	226
S5	13.52	0.04	346
S6	8.75	0.36	24

significantly lower ($p < 0.05$) than the observed NO₃⁻N level. The total soluble P (TSP) was about 88 % of the total P (TP) concentration in the dry deposition samples (Fig. 4). Particulate P (PP) made up the remaining 12 %. Soluble reactive P (SRP) was less than 2 % of the TP and soluble organic P was about 86 % of TP. Mean deposition of TP had a range of 1.18 ± 0.76 to 11.3 ± 17.6 mg m⁻² day⁻¹ with an overall mean value of 4.56 mg m⁻² day⁻¹ (Fig. 4). The total soluble P fraction had more soluble organic P constituent. The levels of the observed P depositions may have been influenced by biomass burning, local fish processing, vehicular activities and modern agriculture practices around the Lagos metropolis. Abayomi et al. (2011) and Schindler et al. (2006) have highlighted some of these factors as contributors to the P pool of an environment. Morales et al. (2001) also ascribed the release of low molecular weight molecules or aerosols by vegetation as an important source of atmospheric P. Mean total soluble P deposition was significantly greater ($p < 0.05$) than dissolved inorganic SRP deposition, indicating that much of the dry deposition was in soluble organic form. This observation has previously been reported by Bootsma et al. (1999) and Morales et al. (2001).

The molar ratios of total N to total P in dry deposition rates are reported in Table 3. They greatly exceeded 22,

ranging from 24 to 346. These very high ratios were due to extremely low P levels in the deposition except site S6 where TN/TP was 24. This may be due to the fact that the sources of NO_x are greater including lightning and microbial processes. Also, biological sources of N and P will normally emit more N than P in accordance with their mass composition.

Significance of differences in the data obtained was determined by one-way repeated-measures analysis of variance (ANOVA) and multiple comparisons were performed by contrasts and post hoc tests. Significance of correlations was carried out with Pearson’s correlation. All raw data were tested for normality (Table 4) before statistical treatment and it was found that only PN and PP data passed the Kolmogorov–Smirnov and the Shapiro–Wilk tests for normality after Lilliefors significance correction for all the raw data. All other data had significantly non-normal distributions ($p < 0.05$). The high standard deviations of the data were responsible for this non-parametric distribution. As a result, the raw data were logarithmically transformed to normalize them. This significantly reduced their skewness and kurtosis. Table 5 compares the skewness and kurtosis of the normalized data to those of skewed raw data.

The linear interrelationship between the studied nutrients is shown in Table 6. Medium positive correlation

Table 4 Tests of normality on the nutrient data obtained in the study

	Kolmogorov–Smirnov ^a			Shapiro–Wilk		
	Statistic	Df	Sig.	Statistic	Df	Sig.
Nitrate-N	0.18	36	0.00	0.87	36	0.00
(NH ₄ ⁺ + organic)-N	0.30	24	0.00	0.61	24	0.00
SRP	0.17	36	0.01	0.85	36	0.00
SOP	0.36	24	0.00	0.42	24	0.00
PN	0.29	6	0.14	0.85	6	0.16
PP	0.17	6	0.20 ^b	0.93	6	0.54

^a Lilliefors significance correction

^b This is a lower bound of the true significance

Table 5 Skewness and kurtosis after transformation of the skewed raw data to normal distribution

Parameter	Raw data		Log-transformed data	
	Skewness	Kurtosis	Skewness	Kurtosis
Nitrate-N	1.16	0.48	0.03	-0.46
[NH ₄ ⁺ + organic]-N	2.50	6.01	-0.80	1.11
SRP	1.45	2.27	1.18	1.25
SOP	4.04	17.32	1.28	1.91
PN	0.48	-2.10	0.12	-2.75
PP	0.52	-1.18	-0.39	-1.90

existed between nitrate and phosphate ($r = 0.38$, $p < 0.05$), between (NH₄⁺+organic)-N and soluble organic P ($r = 0.29$, weak) and between particulate N and particulate P ($r = 0.34$). This is an indication of the parallel relationship between the concentrations of the parameters studied. This may be attributed to similar wind speeds and similar long-range transports influencing their distribution and motion in the atmosphere. Another possible reason for the positive correlations is that the species must have originated from the same secondary transformation processes or same sources in addition to the foregoing reasons. The correlation between nitrate and phosphate was significant ($p < 0.05$) as shown in Fig. 2. This conformed to the findings of Bootsma et al. (1999). Conversely, the correlations between [NH₄⁺+organic]-N and soluble organic P and between particulate N and particulate P were not significant ($p > 0.05$). Negative correlation existed between the

pairs: nitrate versus [NH₄⁺+organic]-N ($r = -0.47$, $p < 0.05$) and phosphate versus soluble organic P ($r = -0.20$). This is so because oxidation or mineralization of the organic species (organic-N and organic-P) decreases its own level and increases the level of the resulting inorganic species (NO₃⁻ and PO₄³⁻) by a proportionate amount, all other things (speed, transport pattern, transformation, distribution and origin) being equal. It is noteworthy that the negative correlation between nitrate and [NH₄⁺+organic]-N was a significant ($p < 0.05$) medium effect. This is an indication of a balance between NO₃⁻, NH₃ and organic-N. On the contrary, the correlation between phosphate and soluble organic P was weak and not significant and the probability that it was due to unsystematic variation was large, 34.5 %.

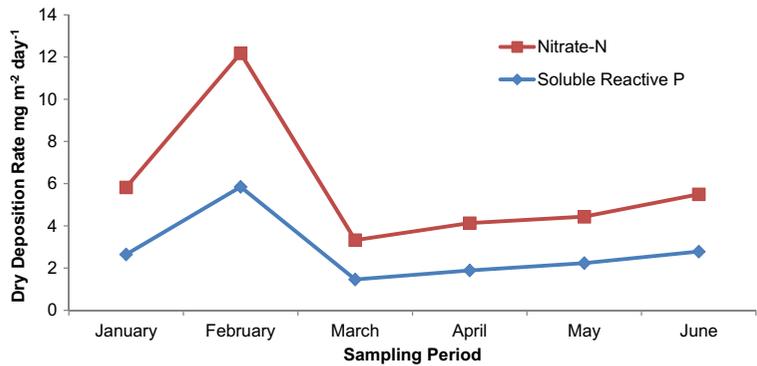
Nitrate and [NH₄⁺+organic]-N (in dissolved condition) were negatively correlated with particulate N.

Table 6 Pearson's correlations

		LogNO ₃	log[NH ₄ ⁺ + organic]-N	LogSRP	logSOP	logPN	LogPP
LogNO ₃	Correlation	1	-0.47*	0.38*	-0.16	-0.38	0.23
	Sig. (two-tailed)		0.02	0.02	0.46	0.46	0.56
log[NH ₄ ⁺ + organic]-N	Correlation	-0.47*	1	-0.14	0.29	-0.54	-0.57
	Sig. (two-tailed)	0.02		0.50	0.17	0.27	0.11
LogSRP	Correlation	0.38*	-0.14	1	-0.20	0.27	-0.02
	Sig. (two-tailed)	0.02	0.50		0.35	0.60	0.95
LogSOP	Correlation	-0.16	0.29	-0.20	1	-0.77	-0.39
	Sig. (two-tailed)	0.46	0.17	0.35		0.08	0.31
LogPN	Correlation	-0.38	-0.54	0.27	-0.77	1	0.34
	Sig. (two-tailed)	0.46	0.27	0.60	0.08		0.52
LogPP	Correlation	0.23	-0.57	-0.02	-0.39	0.34	1
	Sig. (two-tailed)	0.56	0.11	0.95	0.31	0.52	

*Correlation is significant at the 0.05 level (two-tailed)

Fig. 5 Temporal variation of the dry deposition rates



Similarly, phosphate and soluble organic P (in dissolved condition) were negatively correlated with particulate P. The inverse variation is because the more the particulate species goes into solution the lower its concentration in the particulate form becomes and the higher is the concentration of the resultant soluble species. Although most of these negative effects were medium to large, yet they were non-significant. The probabilities of the effects occurring by random errors were generally very large, between 26.7 and 95.2 % (Table 6).

A non-significant positive correlation was observed between pH and nitrate ($r = 0.410, p = 0.05$) and between pH and phosphate ($r = 0.288, p = 0.05$). Although the correlations were statistically ascribed to chance, a positive correlation was expected

between pH and phosphate ions because phosphate, being a conjugate base of a weak acid (H_3PO_4), is a weak base. It will abstract proton from water and generate hydroxide ions via hydrolysis, thereby raising the pH. Increase in pH with a rise in phosphate level is sound but a positive correlation between pH and nitrate must be due to a third-variable problem because nitrate ion is the anion of a strong acid (HNO_3) and will only have negligible tendency to abstract proton from water; the water pH will not be affected (Brown et al. 2009).

Repeated-measures ANOVA was applied to the data and the results were $F(5, 25) = 9.39, p = 0.05$ and $F(5, 25) = 3.20, p = 0.05$ for nitrate and phosphate, respectively. The [ammonium + organic]-N and SOP results were $F(3,$

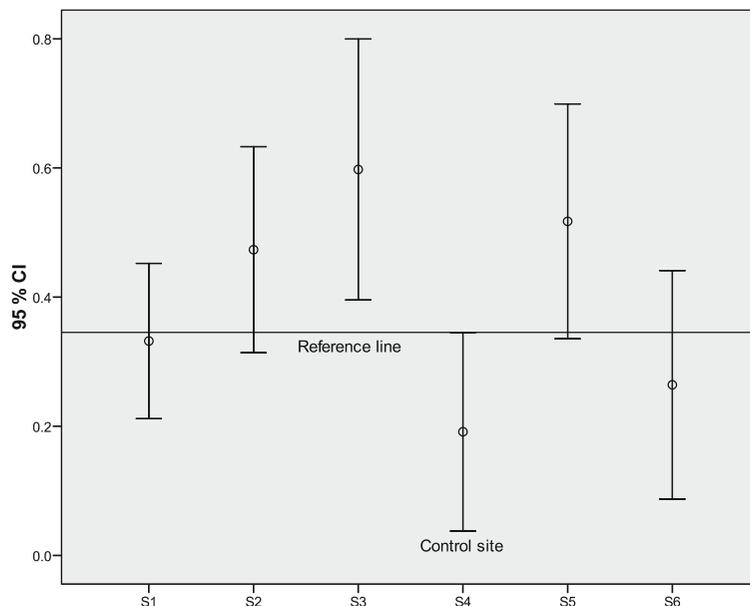
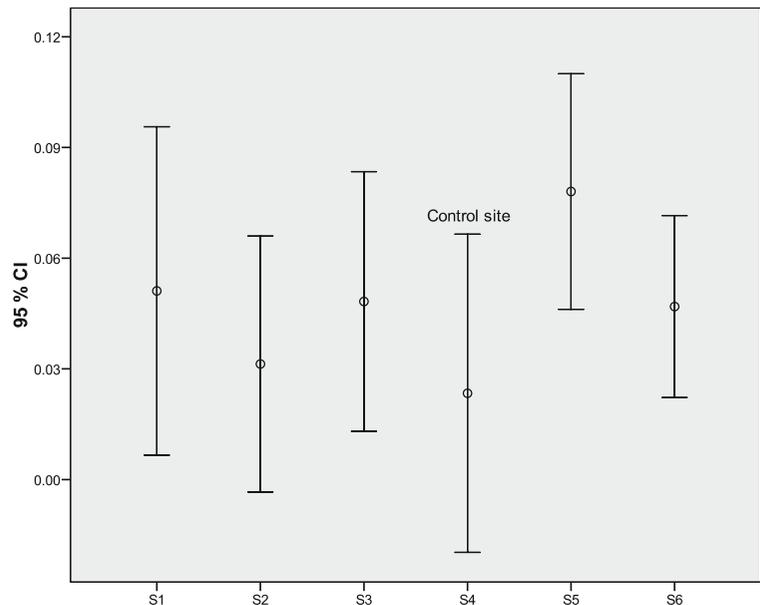


Fig. 6 Error bars showing atmospheric nitrate deposition at the study sites in relation to the control site; reference line distinguishes between the unpolluted sites (control site inclusive) and the polluted sites; CI confidence interval

Fig. 7 Error bars showing atmospheric phosphate deposition at the study sites in relation to the control site; CI confidence interval



15) = 6.07, $p = 0.05$ and $F(5, 25) = 3.28$, $p = 0.05$, respectively. The deposition rates of the entire nutrient species were significantly affected by temporal variation from January to June as their F ratios are significant ($p = 0.05$). The significant temporal variation of the atmospheric deposition was traced by within-subjects contrasts and post hoc tests to significant differences between February data and each of the data for January ($p = 0.04$), March ($p = 0.03$) and April ($p = 0.03$). The temporal variation is graphed below (Fig. 5). It is evident that dry deposition rates were higher in the dry season (January to February) and descended sharply to the wet season (March to June). This supports the findings of contrasts and post hoc tests that the main effect of the variation was due to the significantly higher results of February than January, March and April.

January and February had the highest levels of the nutrients because this period fell within the dry season with few or no rain events such as rainout and washout which would largely lower the deposition rates of the nutrients.

The error bar graph below (Fig. 6) constructed with repeated-measures design predicts that site S3 differed significantly from the control site S4 because their error bars do not overlap. Similarly, S5 sparingly overlapped with S4; its negative cap thinly crossed the reference line. In terms of concentration, the nitrate concentrations of these sites (S3 and S5) and that of the control site did not come from the same population. Other sites

(especially S1 and S6) were predicted to have received nitrate from the same population as the control site because their error bars overlap well. Therefore, the mean nitrate levels of S3 and S5 would differ significantly from the control value. This is an indication of sufficient nutrient deposition or enrichment at S3 and S5. However, S1, S2 and S6 would have non-significantly different nitrate levels from the control value.

When repeated-measures ANOVA was applied to the data, the results obtained were $F(5, 25) = 4.88$, $p = 0.05$. This showed a main effect. The significant difference between the sites was analyzed by within-subjects contrasts and it was found that sites S2, S3, and S5 received significantly higher nitrate depositions ($p = 0.01$, $p = 0.02$ and $p = 0.04$, respectively) than the control site while sites S1 and S6 had nitrate depositions that were not significantly different ($p = 0.12$, $p = 0.48$, respectively) from the control value. These results are in agreement with their error bar predictions (Fig. 6).

Figure 7 shows the error bar graph constructed with repeated-measures design. It shows a non-significant difference in dry phosphate deposition between the study sites and the control site because their error bars overlap very well indicating that their phosphate concentrations came from the same population. Any difference in their concentrations was due to random variation. Repeated-measures ANOVA was applied to the

data and the results obtained were $F(5, 25) = 1.49$, $p > 0.05$. This also reflects a non-significant difference between the six sites as predicted by their error bar graph (Fig. 7).

In addition to bioavailable NO_3^- and SRP, microbial decomposition and oxidation of the deposited SOP, PP, [ammonium + organic]-N and PN in the Lagos Lagoon will alter N and P cycles by increasing nutrient concentrations in the water column and sediment (Bayley et al. 2005) This is expected to have significantly contributed to the eutrophication of the lagoon, whereby there was a shift from clear water state to a hypertrophic state with turbid, coloured water dominated by algae and cyanobacteria. This can retard the growth of normally submerged macrophytes and stimulate the proliferation of floating macrophytes (Geurts et al. 2010) such as water hyacinth which is prevalent in the lagoon.

Conclusions

This study proves that atmospheric deposition of nutrients to the Lagos Lagoon is ongoing. A much larger portion of the dry atmospheric N and P depositions onto the lagoon and its watersheds is in the form of soluble organic compounds, particulate forms and ammonium species. Eventually, these deposited nutrients are leached into the lagoon basin by rainwater runoff and some percentage of the nutrient will percolate into the lagoon from freshwater sources because freshwater systems are phosphorus-limited and will not use the excess nitrogen received from atmospheric deposition and most of the nitrogen will be delivered to estuarine systems. The large quantities of these nutrients represent a significant proportion of the total nutrient loading to the lagoon. The deleterious input of particulate and soluble nutrients to the Lagos Lagoon is evidenced by the proliferation of water hyacinth over the lagoon surface, its huge water-column P level (Abayomi et al. 2011) and water-column hypoxia (Alo et al. 2010).

While the continuous nutrient enrichment of the Lagos Lagoon is driven by numerous sources which are mostly terrestrial, the realization that atmospheric deposition could contribute measurable nutrients into the lagoon portends a new challenge whose control will have to be hinged on multi-faceted approach such as drastic reduction in open waste burning, improved and prompt waste management strategies to discourage decomposition that may instigate large scale NH_3 release and enforcement of extant

regulations on industrial and tail-pipe gaseous emissions. This will go a long way in reducing the amount of nutrients from atmospheric depositions and along with other point source control measures, ensure a progressive reduction in the nutrient levels of the lagoon. This will in turn halt the continuous eutrophication of the water body and engender the regeneration of its resources.

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