Scientific Research Publishing

Journal of Agricultural Chemistry and Environment, 2019, 8, 155-171
http://www.scirp.org/journal/jacen
ISSN Online: 2325-744X
ISSN Print: 2325-7458

Analysis of Iron, Scandium, Samarium, and Zinc in Commercial Fertilizers and the Chemistry behind the Stability of These Metals in the Fertilizers

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How to cite this paper: Rahman, Md.S., Hossain, S.M., Rahman, M.T. and Kabir, M. (2019) Analysis of Iron, Scandium, Samarium, and Zinc in Commercial Fertilizers and the Chemistry behind the Stability of These Metals in the Fertilizers. *Journal of Agricultural Chemistry and Environment*, **8**, 155-171.
https://doi.org/10.4236/jacen.2019.83013

Received: July 1, 2019
Accepted: August 13, 2019
Published: August 16, 2019

Abstract

Fertilizers are the indispensable materials for farming and one of the major components of the current world economy. It is essential to understand the chemical structures of fertilizers to provide best quality products to the consumers. In this study, chemical structures of some frequently used commercial fertilizers (compost, DAP, and TSP) and their phosphate-metal interaction chemistry were studied employing both analytical and theoretical methods. Three types of fertilizer samples from the mid-southern part of Bangladesh were collected to quantify the content of two micronutrient metals (iron and zinc) and two non-essential metals (scandium and samarium). Neutron activation analysis (NAA) coupled with γ-ray spectrometry was employed to analyze the content of the metals where three standard reference materials, namely IAEA-SL-1 (Lake Sediment), IAEA-Soil-7, and NIST Coal Fly Ash 1633b, were used. Concentration of Fe (2964 - 24,485) mg/kg, Sc (3.50 - 11.80) mg/kg, Sm (2.19 - 26.69) mg/kg, and Zn (243 - 4426) mg/kg were determined in the fertilizer samples. Extremely high concentrations of Fe and Zn were quantified in some of the compost and phosphate fertilizers in comparison with other studies of different countries. Quantum mechanical calculations were performed to understand the molecular level interactions of Fe and Zn with triple super phosphate (TSP) and diammonium phosphate (DAP) fertilizers by employing DFT-B3LYP/SDD level theory. Results showed that both Fe and Zn have high affinity with the phosphate fertilizers, but Fe compound showed stronger binding affinity than the Zn compounds, which supported the experimental results. Another interesting finding was that the compounds of Fe and Zn attached to the oxygen of the phosphate group of the fertilizers by covalent-like bonding. HOMO-LUMO gaps of the Fe-DAP/TSP complexes were observed significantly lower than the Zn-DAP/TSP, which also demonstrated that Fe compound could have higher affinity to attach with the phosphate group of DAP and TSP fertilizers.

Keywords

Phosphate Fertilizer, NAA, γ-Ray Spectrometry, Metal-Phosphate Interaction, DFT

1. Introduction

Fertilizers are indispensable materials, providing essential nutrients to soil to maximize food production. Fertilizers are becoming one of the essential factors of the world economy [1]. So, it is easily comprehensible that the need for fertilizer is increasing tremendously. World demand for phosphate fertilizers was 41,700,000 tons in 2013, but it is expected to become 46,600,000 tons by 2018 [1]. Among the phosphate fertilizers, DAP and TSP are the most consumed fertilizers [2], because both can supply high content of phosphorous, where DAP can also provide high amount of nitrogen [3]. Manufacturers sometimes mix high amounts of phosphate ores and recycled by-products to the fertilizers to meet the nutritional needs of soil [4] [5]. In this way, excessive amount of trace metals could be ingested into the fertilizers. The common forms of those metals in the fertilizers are oxides and sulphates [6] [7]. Since some of these metallic compounds show great affinity to the phosphate groups, after the application of the phosphate fertilizers, those compounds could retain in the topsoil for a longer period of time [8]. Moreover, metals could also stay in soil and water for an extended period of time by changing their oxidation state and worsening the soil environment [9]. Every stakeholder should maintain the quality of the fertilizers, starting from manufacturing process to packaging and must state quality control results on their packages according to the suggestion and trend reported by international regulatory bodies such as FAO, USGS, or USDA [1] [10] [11] [12]. In this study, excessive amount of micronutrient metals, e.g. Fe and Zn detected in some of the fertilizer samples. Therefore, this study tried to find out the reasons behind the high concentration of the metals in the phosphate fertilizer samples by employing density functional theory calculations.

It is important to know because excessive exposure of the essential nutrient metals could cause severe environmental and health hazards. Elevated level of Fe can cause "Bronzing" of the rice leaves, which reduces the rice-yield; it can even cause complete crop failure [13]. Zinc is also an essential trace element since it has the antagonistic capacity against copper and cadmium toxicity [14] [15], but application of large doses of zinc over extended periods of time by diverse sources such as fertilizers, pesticides, and manure could cause Zn induced iron deficiency-chlorosis. When plant leaves exceed 500 mg Zn/kg DW then it could cause phytotoxicity [16].

Scandium and samarium metals do not get absorbed by the plants to a measurable extent, so these metals should not have any significant role in agricultural soil and the human diet, but Rim *et al.* [17] reported that samarium could be slightly toxic in its soluble form.

Quantification of metal contents in diversified types of samples can be accomplished by various methods such as Inductively Coupled Plasma-Atomic Emission Spectrometry (ICPAES) [18], Continuum Source Graphite Furnace Atomic Absorption Spectrophotometry (CS-GFAAS) [19], Wavelength Dispersive X-Ray Fluorescence Spectrometry (WD-XRF) [20], Proton-Induced X-ray Emission (PIXE) [21], and Neutron Activation Analysis (NAA) [8]. Each method has its own advantages and disadvantages, but NAA method was used in this study because it needs no chemical treatment, non-destructive, matrix independent only based on the (n, γ) nuclear reaction, and IAEA regarded it as a "Reference Method" [22]. The only difficulty to run this method could be its overall cost.

Density functional theory (DFT) is one of the most effective ways to study different chemical, material, and biological system [23]. To comprehensively understand the structural changes, binding energy changes, and other modifications occurred by strong interaction of metallic compounds with fertilizers, DFT calculations can play a successful role [8].

In this study, we investigated Fe, Sc, Sm, and Zn contents in frequently used commercial fertilizers from the mid-southern region of Bangladesh employed by neutron activation analysis (NAA). In addition, quantum mechanical calculations revealed the structural characteristics of the fertilizers, TSP and DAP, and the compounds interacting with them. The structural changes occurred in fertilizers due to the interaction of Fe and Zn compounds, and the reasons behind the compounds high affinity to the fertilizers were explored.

2. Materials and Methods

2.1. Sample Collection

The detail method of sample collection was explained in our earlier study [8]. Concisely, total ten phosphate (TSP and DAP) and compost fertilizer samples were collected to observe the level of essential (Fe and Zn) and non-essential metals (Sc and Sm) from the mid-southern part of Bangladesh namely; Alfadanga and Shaltha in Faridpur, Agargaon, Mirpur-2 (Kingshook Nursery), Savar (Gerua Bazar) in Dhaka, and Mohammadpur in Magura [8]. Sample identification numbers were assigned as, C11-L, C13L, C14-L, T22-L, T32-L, T42-L, T52-L, T62-L, D24-L, and D54-L where C, T, and D means compost, TSP, and DAP, respectively. Coordination data of the sample collection points are presented in **Table S1**.

2.2. Sample Preparation for INAA Analysis

Sample preparation and correction of the interference were also described in the previous study [8]. In brief, collected samples were taken into an electric oven to dry about 65˚C until having constant weight. About 60 mg of dried, homogeneous, and powdered fertilizer samples were heat sealed in a small polyethylene bag. Three standard reference materials (SRMs) were used where IAEA-Soil-7 was used as a standard, and IAEA-SL-1, NIST-1633b (Coal Fly Ash) were used as the control samples. Three 0.1 mm thick Al-Au foil monitor foils were placed within the sample pile and irradiated those along with the samples to determine the neutron flux gradient. Three megawatt (MW) TRIGA Mark–II research reactor was used in this nondestructive relative standardization approach. Long irradiation of reference materials and samples in the rotary specimen rack applying 5.07×10^{13} $\text{ncm}^{-2}\cdot\text{sec}^{-1}$ thermal neutron flux for 6 minutes at 2.4 MW was conducted. A pre-calibrated HPGe detector [CANBERRA, 25 % efficiency relative to a NaI (Tl) detector, 1.8 keV resolution at 1332.5 keV of ^{60}Co] connected to a digital gamma spectrometer (ORTEC, DSPEC Jr$^{\text{TM}}$) was used. The γ-rays emitted from both the samples and standards were measured at the same geometry. The dead time of the detector was kept below 15%.

Two steps of counting were performed for the long irradiation. The first counting was performed to determine Sm content in samples, standard, and controls after a decay time of 1 day, with the lifetime of 1800 - 3000 s with the acquisition software Maestro-32 (ORTEC). The second counting was conducted after 3 weeks with the lifetime of 7200 s for the determination of Fe, Sc, and Zn.

2.3. Quality Control and Detection Limit

Ratio of the measured concentrations of the studied metals in control samples (NIST-1633b Coal Fly Ash and IAEA-SL-1) to their certified concentrations gave a strong quality control result for this experiment (**Figure S1(a)** and **Figure S1(b)**). Deviations were found within 5% for most of the metals in both cases except Sm in SL-1 had 12% deviation, and the deviation calculated for Zn in NIST 1633b was 28%. Overall, the QC results provided reliability of the calculated results. A three-σ criterion [8] was employed to calculate the detection limit of studied metals (**Table S2**).

2.4. Computational Method

Gaussian 09 software package [24] was used to optimize the structures of DAP and TSP and their complexes with $FeSO_4$, ZnO, and $ZnSO_4$ at gas phase. Vibrational frequencies were calculated with the density functional theory (DFT) employing (BLYP) correlation functional [25]. All calculations were conducted by SDD basis set, which can produce reliable results for the interaction between metallic compounds and phosphate fertilizers [8] [26]. After computing, several thermochemical properties such as change of electronic energies, enthalpies, Gibbs free energies, HOMO-LUMO gaps, dipole moments, hardness and softness of the fertilizers, and the fertilizer-metal complexes were investigated.

3. Results and Discussion

3.1. Iron and Zinc Content in Compost, TSP, and DAP

The concentrations of iron in compost, TSP, and DAP are 13,206.783 - 24,484.775 mg/kg, 2963.809 - 19,615.839 mg/kg, and 18,398.228 - 23,403.794 mg/kg, respectively (Figure 1(a)). All compost samples contain the concentration of iron are (C11-L = 13,512.279 ± 457.814 mg/kg; C13L = 24,484.775 ± 740.027 mg/kg, C14-L = 13,206.783 ± 462.619 mg/kg); TSP samples (T22-L = 3806.085 ± 202.853 mg/kg, T32-L = 3435.955 ± 193.816 mg/kg, T42-L = 19615.839 ± 623.845 mg/kg, T52-L = 4147.968 ± 212.192 mg/kg, T62-L = 2963.809 ± 176.921 mg/kg); and DAP samples (D24-L = 18,398.228 ± 598.977 mg/kg, D54-L = 23,403.794 ± 695.150 mg/kg). Concentration of Fe in DAP and compost seems remarkably higher than the other studies such as Chile and Egypt (Table 1). The ranges of iron concentration in soil samples of Punjab (India) reported 2800.0 - 5700.0 mg/kg (Table S3). Therefore, the repeated use of extremely high iron-enriched fertilizers could be turned into beneficiary evil.

Table 1. Ranges and mean concentration of Fe (mg/kg), Sc (mg/kg), Sm (mg/kg), and Zn (mg/kg) in phosphate fertilizers of different countries.

Region/ Country	Number of Samples	Types	Ranges Fe (mg/kg)	Mean Fe (mg/kg)	Ranges Zn (mg/kg)	Mean Zn (mg/kg)	References
Chile	12	TSP	5200.0 - 6800.0	6000.0	43.0 - 883.0	600.0	[29]
		DAP	7100.0 - 11,000.0	9100.0	38.1 - 44.5	41.3	
Egypt	-	Superphosphate		7600.0		107.80	[28]
Europe (12 Countries)	196	Phosphate	-	-	-	166.0	[27]
		TSP	2963.81 - 19,615.84	6793.93	243.33 - 472.52	346.73	This study
Bangladesh	10	DAP	18,398.23 - 23,403.79	20,901.01	348.14 - 4426.17	2387.15	
		Compost	13,206.78 - 24,484.78	17,067.95	312.73 - 3359.90	1511.22	
			Ranges Sc (mg/kg)	**Mean Sc (mg/kg)**	**Ranges Sm (mg/kg)**	**Mean Sm (mg/kg)**	
Pakistan	-	SSP	-	-	-	2.02	[41]
		DAP	-	-	-	12.0	
Brazil	-	SSP		24.6		122.0	[36]
Brazil	-	MAP		-		43.0	[41]
		TSP		-		89.0	
Egypt	-	Superphosphate	-	3.99	-	-	[28]
Bangladesh		TSP	5.74 - 11.80	7.92	6.38 - 26.69	14.807	This study
	10	DAP	6.97 - 8.42	7.694	6.58 - 7.22	6.902	
		Compost	3.50 - 7.09	4.785	2.19 - 3.88	3.075	

The concentration ranges of zinc in compost, TSP, and DAP fertilizers are 312.734 - 3359.896 mg/kg, 243.327 - 472.515 mg/kg, and 348.135 - 4426.172 mg/kg, respectively (**Figure 1(d)**). All compost samples (C11-L = 3359.896 ± 193.670 mg/kg, C13-L = 861.017 ± 46.716 mg/kg and C14-L = 312.734 ± 19.156 mg/kg); TSP samples (T22-L = 262.236 ± 16.421 mg/kg, T32-L = 243.327 ± 17.541 mg/kg, T42-L = 398.272 ± 26.452 mg/kg, T52-L = 357.313 ± 24.710 mg/kg, T62-L = 472.515 ± 31.520 mg/kg); and DAP samples (D24-L = 348.135 ± 23.588 mg/kg, D54-L = 4426.172 ± 259.968 mg/kg) contain Zn in extremely high concentration compared to the European and Egypt market, specially C11-L, C13-L, T52-L, and D54-L.

The average Zn concentration in the phosphate fertilizers in European market was reported 166 mg/kg [27] where average Zn content in superphosphate fertilizer of Egypt market was 107.80 mg/kg [28] and Zn content in phosphate fertilizers of Chile market was 41.3 to 600.0 mg/kg [29]. So, the concentrations of Zn in sample C11-L and D54-L were found about 20 times and 27 times higher than the European market, respectively.

Zinc is unevenly distributed in soil and its concentration ranges between 73.0 to 320.0 mg/kg in Punjab (India) [30]. Kabata-Pendias and Pendias [31] stated that calcareous soils and organic soils can contain the highest background Zn contents. Moreover, several studies of USA and European countries reported that average concentration of Zn in soil can vary between <3 and 264 mg/kg in **Table S3** [31] [32] [33] [34]. Besides concentration of Zn found in agricultural soils of Japan is 2.5 to 330 mg/kg [35]. On that account, some of the fertilizer samples contain extremely high amounts of Zn.

3.2. Scandium and Samarium Content in Compost, TSP, and DAP

The concentrations of scandium in compost, TSP, and DAP are 3.496 - 7.092 mg/kg, 5.735 - 11.796 mg/kg, and 6.965 - 8.423 mg/kg, respectively (**Figure 1(b)**). All compost samples contain the concentration of scandium are (C11-L = 3.767 ± 0.248 mg/kg, C13-L = 7.092 ± 0.461 mg/kg and C14-L = 3.496 ± 0.230 mg/kg);

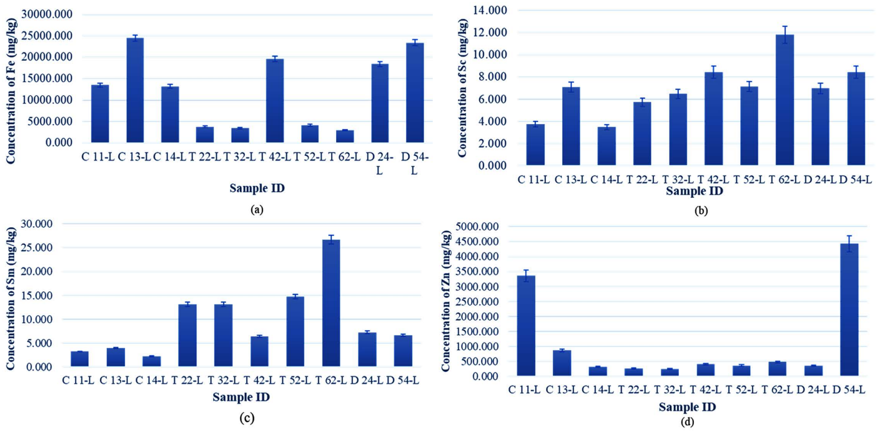


Figure 1. Concentration of (a) Fe (iron), (b) Sc (scandium) (c) Sm (samarium), and (d) Zn (zinc) in studied samples where C = Compost, T = TSP, and D = DAP.

TSP samples (T22-L = 5.735 ± 0.374 mg/kg, T32-L = 6.478 ± 0.422 mg/kg, T42-L = 8.432 ± 0.548 mg/kg, T52-L = 7.139 ± 0.465 mg/kg, T62-L = 11.796 ± 0.764 mg/kg); and DAP samples (D24-L = 6.965 ± 0.454 mg/kg, D54-L = 8.423 ± 0.547 mg/kg). Turra *et al.*, 2011 reported the mean concentration of Sc in SSP fertilizers of Brazil is 24.6 mg/kg. Besides, the range of the mean concentrations of Sc in the soil reported in the studies of countries across the world is 6.1 to 18.0 mg/kg [36] [37] [38] [39] [40] (**Table S3**). These results showed that estimated Sm contents in the fertilizer samples are within normal limit.

Additionally, the ranges of Sm concentration in compost, TSP and DAP were measured as 2.186 - 3.879 mg/kg, 6.381 - 26.694 mg/kg, and 6.581 - 7.223 mg/kg, respectively. Average concentration of Sm in the studied fertilizer samples are less than most of the studies reported in **Table 1** except Pakistan [28] [36] [41] [42]. All compost samples (C11-L = 3.161 ± 0.109 mg/kg, C13-L = 3.879 ± 0.134 mg/kg and C14-L = 2.186 ± 0.076 mg/kg); TSP samples (T22-L = 13.138 ± 0.453 mg/kg, T32-L = 13.121 ± 0.452 mg/kg, T42-L = 6.381 ± 0.220 mg/kg, T52-L = 14.703 ± 0.507 mg/kg, T62-L = 26.694 ± 0.921 mg/kg); and DAP samples (D24-L = 7.223 ± 0.249 mg/kg, D54-L = 6.581 ± 0.227 mg/kg) contain Sm within the expected limit compared to the other studies.

3.3. Interaction and Binding of Fe and Zn with TSP

Equilibrium geometry and the optimized structures of TSP and its complexes TSP-FeSO$_4$, TSP-ZnO, and TSP-ZnSO$_4$ are presented in **Figure 2**. Chosen bond distances and angles of the complexes are summarized in **Table 2** (atom numbers are indicated in the optimized structures). Few significant changes were occurred compared in the structure of TSP when it forms complex with ZnO. In ZnO-TSP, Ca(15)-O(10) elongated from 2.32 Å to 4.17 Å. To compare the structural changes in TSP-FeSO$_4$ and TSP-ZnSO$_4$, bond distances between Fe

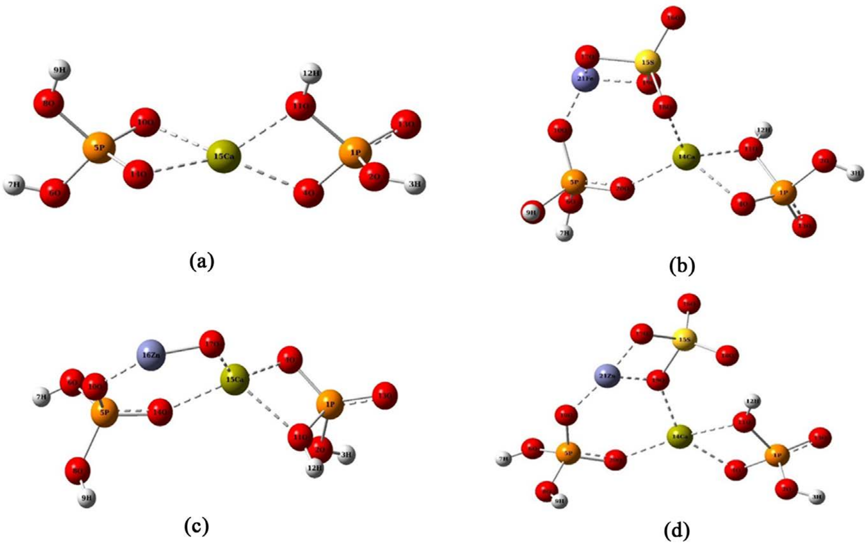

(a)
(b)
(c)
(d)

Figure 2. Optimized structures of (a) TSP; (b) TSP-FeSO$_4$; (c) TSP-ZnO; and (d) TSP-ZnSO$_4$ computed at B3LYP/SDD level of theory.

Table 2. Selected bond distances (Å) and angles (˚) of TSP-metal complexes calculated at B3LYP/SDD level of theory.

Assignment	TSP	Assignment	TSP-$FeSO_4$	Assignment	TSP-ZnO	Assignment	TSP-$ZnSO_4$
Ca(15)-O(4)	2.22	Ca(14)-O(4)	2.22	Ca(15)-O(4)	2.25	Ca(14)-O(4)	2.21
Ca(15)-O(10)	2.32	Ca(14)-O(10)	4.08	Ca(15)-O(10)	4.17	Ca(14)-O(10)	4.20
Ca(15)-O(11)	2.34	Ca(14)-O(11)	2.35	Ca(15)-O(11)	2.37	Ca(14)-O(11)	2.30
Ca(15)-O(14)	2.32	Ca(14)-O(18)	2.39	Ca(15)-O(14)	2.30	Ca(14)-O(19)	2.27
P(5)-O(10)	1.63	P(5)-O(10)	1.63	P(5)-O(10)	1.65	P(5)-O(10)	1.64
P(5)-O(8)	1.70	P(5)-O(8)	1.68	P(5)-O(8)	1.68	P(5)-O(8)	1.68
P(5)-O(6)	1.68	P(5)-O(6)	1.66	P(5)-O(6)	1.67	P(5)-O(6)	1.67
P(1)- O(13)	1.57	P(1)-O(13)	1.57	P(1)-O(13)	1.57	P(1)-O(13)	1.57
		Fe(21)-O(10)	1.82	Zn(16)-O(10)	1.89	Zn(21)-O(10)	1.85
				Ca(15)-O(17)	2.17		
<O(10)-Ca(15)-O(4)	140.77	<O(10)-Ca(14)-O(4)	150.17	<O(10)-Ca(15)-O(4)	152.69	<O(10)-Ca(14)-O(4)	157.12
<O(14)-Ca(15)-O(11)	127.08	<O(18)-Ca(14)-O(11)	125.17	<O(1)-Ca(15)-O(11)	117.70	<O(19)-Ca(14)-O(11)	83.24
<O(6)-P(5)-O(10)	113.38	<O(6)-P(5)-O(10)	104.77	<O(6)-P(5)-O(10)	110.84	<O(6)-P(5)-O(10)	110.54
<O(8)-P(5)-O(14)	114.98	<O(8)-P(5)-O(20)	111.70	<O(8)-P(5)-O(14)	115.80	<O(8)-P(5)-O(20)	115.64
<O(4)-P(1)-O(13)	125.90	<O(4)-P(1)-O(13)	125.51	<O(4)-P(1)-O(13)	126.07	<O(4)-P(1)-O(13)	125.22

or Zn to the oxygen of the phosphate group of TSP could follow. It was observed from the optimized structure that bond distance between Fe to oxygen of PO_4 was shorter, which is Fe(21)-O(10) 1.82 Å than Zn(21)-O(10) 1.85 Å. It could be an evidence of the strong interaction between Fe and PO_4.

Remarkable changes were seen in bond angles of TSP when formed complex with ZnO. <O(10)-Ca(15)-O(4), <O(14)-Ca(15)-O(11), and <O(6)-P(5)-O(10) bond angles of TSP were changed in TSP-ZnO complex. Due to strong interaction between TSP-ZnO complexes, phosphate group of TSP was flipped compared to the position of the PO_4 in TSP structure.

Differences of binding energy, enthalpy, and Gibbs free energy are listed in **Table 3**. For TSP-$FeSO_4$, the binding energy, enthalpy, and Gibbs free energy changes are −343.941, −346.303, and −297.207 KJ/mol. On the other hand, for TSP-ZnO, the levels are −351.292, −353.655, and −307.709 KJ/mol, for TSP-$ZnSO_4$ the levels are −432.682, −435.308, and −377.284 KJ/mol, respectively. Results suggested that the complexes are thermodynamically stable.

Frontier molecular orbitals (MO) *i.e.*, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and their energy gaps are essential factors to measure the chemical reactivity, extent of affinity and kinetic stability of a complex compound [8]. Larger HOMO-LUMO gap of the complexes means high kinetic stability but low chemical reactivity. In that case, an electron requires high energy to be promoted from HOMO to a relatively high-energy level LUMO. The HOMO and LUMO energy gaps of all metal compounds, TSP, and TSP-metal complexes are summarized in **Table 4** and **Figure 3**.

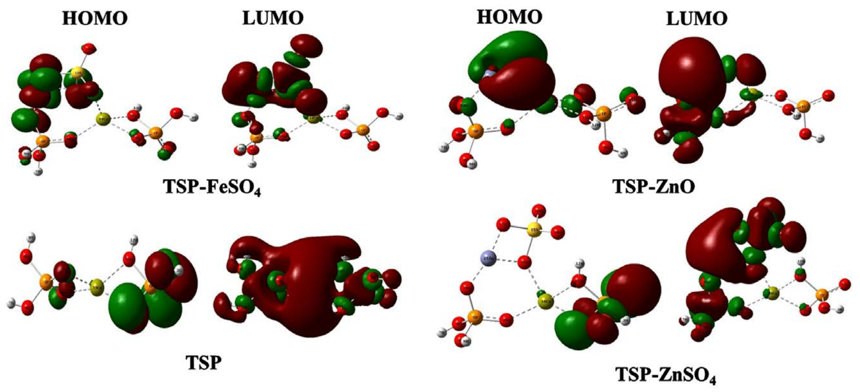


Figure 3. Frontier molecular orbitals (HOMO and LUMO) of TSP and TSP-metal complexes calculated at B3LYP/SDD level of theory.

Table 3. Differences of electronic energies (KJ/mol), enthalpies (KJ/mol), and Gibbs free energies (KJ/mol) of the TSP-metal complexes and DAP-metal complexes calculated at B3LYP/SDD level of theory.

	TSP-$FeSO_4$	**TSP-ZnO**	**TSP-$ZnSO_4$**
ΔE	−343.941	−351.292	−432.682
ΔH	−346.303	−353.655	−435.308
ΔG	−297.207	−307.709	−377.284
	DAP-$FeSO_4$	**DAP-ZnO**	**DAP-$ZnSO_4$**
ΔE	−377.809	−379.122	−429.532
ΔH	−380.172	−381.485	−431.950
ΔG	−321.099	−342.890	−367.045

Table 4. Dipole moments (Debye), energies (eV) of HOMO and LUMO orbitals, HOMO-LUMO gaps (eV), and hardness (eV) and softness (eV) of metal compounds, TSP-metal complexes and DAP-metal complexes are calculated at B3LYP/SDD level of theory.

Combinations	Dipole Moment (Debye)	HOMO (eV)	LUMO (eV)	HOMO-LUMO Gap (eV)	Hardness (eV)	Softness (eV)
$FeSO_4$	4.9631	−8.0148	−4.6970	3.3178	1.6595	0.6026
ZnO	5.0264	−7.2905	−4.2994	2.9911	1.4956	0.6686
$ZnSO_4$	7.0110	−8.3397	−5.6224	2.7173	1.3587	0.7360
TSP	5.3899	−8.0676	−1.9138	6.1538	3.0769	0.3250
TSP-$FeSO_4$	5.5839	−7.7172	−3.8969	3.8203	1.9102	0.5235
TSP-ZnO	9.8717	−7.1171	−2.8196	4.2975	2.1488	0.4654
TSP-$ZnSO_4$	12.073	−7.6456	−3.4025	4.2431	2.1216	0.4713
DAP	5.0713	−7.1400	−0.4327	6.7073	3.3537	0.2982
DAP-$FeSO_4$	5.1759	−6.2545	−2.2202	4.0343	2.0172	0.4957
DAP-ZnO	8.1366	−6.7022	−1.2580	5.4442	2.7221	0.3674
DAP-$ZnSO_4$	7.3715	−7.6206	−2.1766	5.4440	2.7220	0.3673

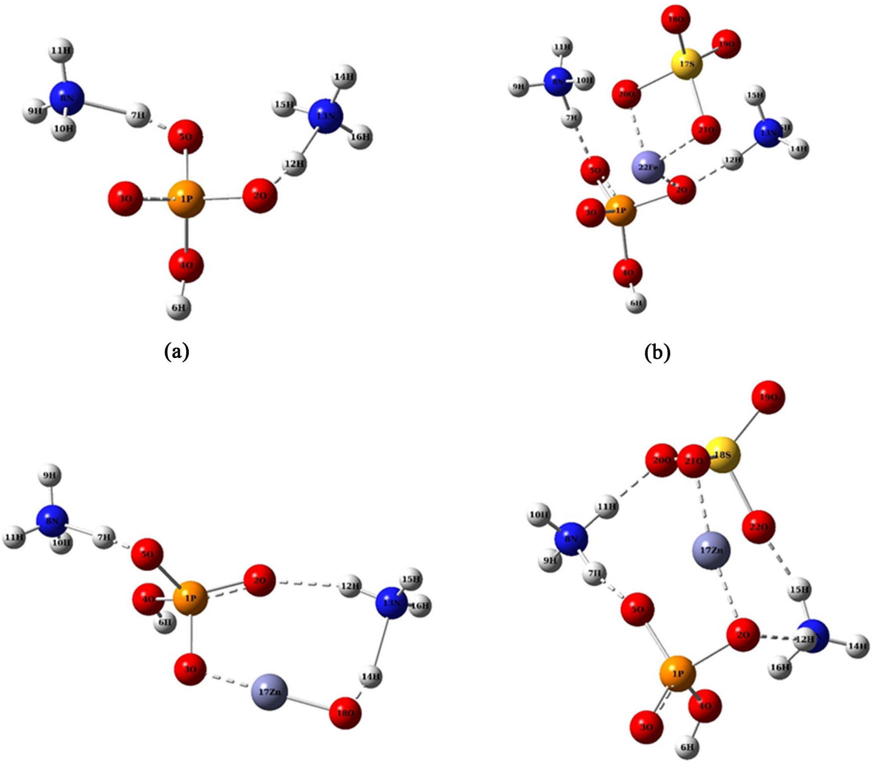
It was observed that Fe has a noticeable effect on the frontier molecular orbital energies. Compared to the TSP, the HOMO and LUMO energy gaps of the Fe-TSP and Zn-TSP complexes had significantly decreased. Among these, Fe-TSP has the least HOMO-LUMO gap. The HOMO and LUMO energy gap of the TSP, TSP-$FeSO_4$, TSP-ZnO, and TSP-$ZnSO_4$ complexes are 6.1538, 3.8203, 4.2975, 4.2431 (eV), respectively, where dipole moments of these complexes are 5.3899, 5.5839, 9.8717, 12.073 (Debye), respectively. Moreover, Fe-TSP complex structure is softer than the Zn-TSP complexes (Table 4). These results confirmed that Fe-TSP complex is more reactive and stable than Zn-TSP complexes.

3.4. Interaction and Binding of Fe and Zn with DAP

Equilibrium geometry and the optimized structures of DAP and its complexes DAP-$FeSO_4$, DAP-ZnO, and DAP-$ZnSO_4$ are depicted in Figure 4. Selected bond distances and angles of the complexes are summarized in Table 5 (atom numbers are shown in the optimized structures). In the structure of DAP-ZnO, few significant changes were occurred compared to the structure of DAP. O(5)-H(7) and O(2)-H(12) bonds got elongated from 1.07 Å to 1.39 Å and 1.09 Å to 2.03 Å. Zn oxide showed strong affinity to the PO_4 of DAP since bond distance between Zn and O of the phosphate group of DAP (Zn(17)-O(3)) is only 1.85 Å. Due to the strong attraction, P(1)-O(3) bond of PO_4 of DAP-Zn had changed significantly. Besides this, the bond distance of Fe(22)-O(2) 1.95 Å in DAP-$FeSO_4$ is shorter than Zn(17)-O(2) 1.97 Å in DAP-$ZnSO_4$. This result implies that the affinity of Fe and phosphate group of the fertilizers are stronger than Zn-phosphate interaction. Therefore, P(1)-O(3) of DAP-$FeSO_4$ got elongated from 1.59 Å 1.66 Å (Table 5).

Table 5. Selected bond distances (Å) and angles (˚) of DAP-metal complexes calculated at B3LYP/SDD level of theory.

Assignment	DAP	Assignment	DAP-$FeSO_4$	Assignment	DAP-ZnO	Assignment	DAP-$ZnSO_4$
N(8)-H(7)	1.53	N(8)-H(7)	1.10	N(8)-H(7)	1.39	N(8)-H(7)	1.09
N(13)-H(7)	1.47	N(13)-H(7)	1.10	N(13)-H(14)	1.79	N(13)-H(7)	1.05
O(5)-H(7)	1.07	O(5)-H(7)	1.51	O(5)-H(7)	1.39	O(5)-H(7)	1.51
O(2)-H(12)	1.09	O(2)-H(12)	1.48	O(2)-H(12)	2.03	O(2)-H(12)	1.80
P(1)-O(5)	1.68	P(1)-O(5)	1.60	P(1)-O(5)	1.63	P(1)-O(5)	1.67
P(1)-O(2)	1.65	P(1)-O(2)	1.70	P(1)-O(2)	1.60	P(1)-O(2)	1.69
P(1)-O(3)	1.59	P(1)-O(3)	1.66	P(1)-O(3)	1.67	P(1)-O(3)	1.57
		Fe(22)-O(3)	1.97	Zn(17)-O(3)	1.85	Zn(17)-O(2)	1.97
		Fe(22)-O(2)	1.95	Zn(17)-O(18)	1.77	Zn(17)-O(21)	1.95
O(5)-P(1)-O(3)	112.98	O(5)-P(1)-O(3)	117.35	O(5)-P(1)-O(3)	111.83	O(5)-P(1)-O(3)	121.09
O(5)-P(1)-O(2)	103.86	O(5)-P(1)-O(2)	114.51	O(5)-P(1)-O(2)	119.42	O(5)-P(1)-O(2)	95.63
O(3)-P(1)-O(2)	118.38	O(3)-P(1)-O(2)	93.71	O(3)-P(1)-O(2)	106.53	O(3)-P(1)-O(2)	123.38



(a) (b) (c) (d)

Figure 4. Optimized structures of (a) DAP; (b) DAP-FeSO4; (c) DAP-ZnO; and (d) DAP-ZnSO4 computed at B3LYP/SDD level of theory.

Moreover, remarkable changes were seen in bond angles. Specially, <O(5)-P(1)-O(2), <O(3)-P(1)-O(2) bond angles of PO_4 in DAP were 103.86˚ and 118.38˚, which had changed significantly by the strong interaction of Fe and Zn compounds (Table 5 and Figure 4). So, both Fe and Zn metals have a strong affinity to the oxygen of PO_4 group. HOMO-LUMO gap, dipole moment change, and hardness and softness of the complexes (Table 4) could help to understand the interactions more comprehensively.

Electronic energy, enthalpy, and Gibbs free energy of metal-fertilizer complexes are summarized in Table 3. As predicted, the difference of electronic energy, enthalpy, and Gibbs free energy of DAP-$FeSO_4$ are −377.809, −380.172, and −321.099 KJ/mol. On the other hand, for DAP-ZnO, the levels are −379.122, −381.485, and −342.890 KJ/mol; for DAP-$ZnSO_4$, the levels are −429.532, −431.950, and −367.045 KJ/mol, respectively. This suggests that the complexes are thermodynamically stable. Moreover, binding energies also recommend that the affinity of between Fe and Zn compounds toward DAP is strong. The HOMO and LUMO energies of all DAP and DAP-metal complexes are summarized in Table 4 and Figure 5. It was observed that Fe has a significant effect on the frontier molecular orbital energies. Compared to DAP, the HOMO and LUMO energy gaps of the Fe-DAP and Zn-DAP complexes are significantly decreased where the HOMO-LUMO gap of Fe-DAP was least. The HOMO and LUMO energy gap of the DAP, DAP-$FeSO_4$, DAP-ZnO, and

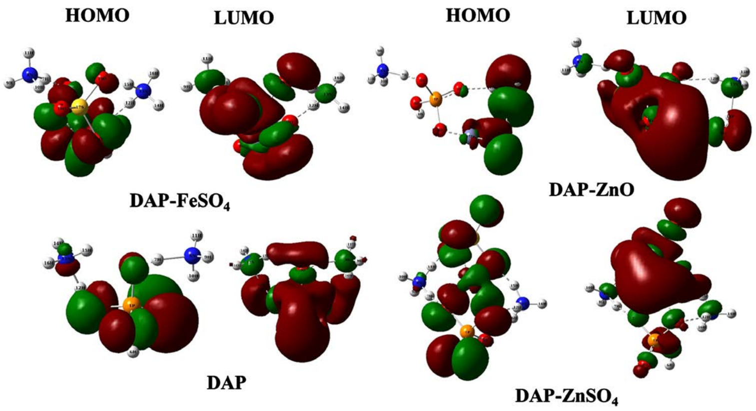


Figure 5. Frontier molecular orbitals (HOMO and LUMO) of DAP and DAP-metal complexes calculated at B3LYP/SDD level of theory.

DAP-ZnSO$_4$ complexes are 6.7073, 4.0343, 5.4442, and 5.4440 eV, respectively. The results suggest that Fe-complex is chemically more reactive to DAP than Zn-complexes. Dipole moments of these complexes are 5.0713, 5.1759, 8.1366, and 7.3715 Debye, respectively. Trend of the dipole moment is also proving the earlier assumption. Moreover, Fe-DAP complex structure is softer than the Zn-DAP complexes (Table 4).

Therefore, quantum mechanical calculation confirmed that both Fe-DAP/TSP and Zn-DAP/TSP complexes are thermodynamically stable, which supports experimental results. It was also observed that Fe-DAP/TSP complexes are more reactive and stable than Zn-DAP/TSP complexes because Fe-DAP complex has lower HOMO-LUMO gap and Fe-PO$_4$ bond distance is smaller than the Zn-PO$_4$.

4. Conclusion

Concentrations of essential metals, Fe and Zn, in some of the fertilizer samples were found to be surprisingly high. Density functional theory revealed that Fe and Zn have strong affinity with the PO$_4$ group present in DAP and TSP. It was proved because both Fe and Zn with the oxygen of the PO$_4$ group formed covalent like bonding, and the complexes were found thermodynamically stable. HOMO-LUMO gap indicated that Fe compound was more prone to attach with the PO$_4$ group of the fertilizers due to lower HOMO-LUMO gap than Zn-fertilizer complexes. Therefore, the combined experimental and theoretical studies revealed that excess Fe and Zn could be stayed with fertilizers in the soil over a long period, gradually be bioaccumulated by the application of either excess phosphate fertilizers or excess metal ingested fertilizers, and eventually could go into food web.

Acknowledgements

The authors are grateful to the Director, INST and Head, Reactor and Neutron Physics Division, INST, AERE, Bangladesh for their permission to use the NAA laboratory facilities. Besides, all authors are also grateful to Dr. Mohammad A.

Halim, CEO of the Red-Green Research Centre (RGRC) for giving permission to use the computational chemistry lab facilities of RGRC (http://grc-bd.org/donate/).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Supporting Information

Table S1. Coordination data of the sample collection area of the mid-southern part of Bangladesh.

Locations of the Study	Coordination	
Agargaon	23°46'45.1"N	90°22'25.17"E
Mirpur-2	23°48'17"N	90°21'48"E
Savar	23°51'29.88"N	90°16'0.12"E
Alfadanga	23°17'0"N	89°43'0"E
Mohammadpur (Magura)	23°24'18"N	89°36'18"E
Saltha	23°24'21.8"N	89°47'39.4"E
Agargaon	23°46'45.1"N	90°22'25.17"E
Mirpur-2	23°48'17"N	90°21'48"E

Table S2. Detection limits of the studied metals.

Elements	Detection Limit (mg/kg)
Fe	410.00
Sc	0.079
Sm	0.024
Zn	28.49

Table S3. Ranges and mean concentrations of Fe (mg/kg), Zn (mg/kg), Sc (mg/kg), and Sm (mg/kg) in the soil of different countries.

Region/ Country	Ranges Sc (mg/kg)	Mean Sc (mg/kg)	Ranges Sm (mg/kg)	Mean Sm (mg/kg)	References
USA	2.8 - 17	9.9	5.2 - 6.6	5.9	[37]
Germany	0.8 - 15	6.1	0.5 - 8.7	3.8	[38]
Australia	-	-	0.4 - 4.6	2.8	[39]
China	11 - 13	12	1.2 - 7.8	5.2	
Japan	0.4 - 56	17	0.2 - 30	3.8	[38]
Brazil	6.6 - 30	18	0.4 - 6.7	3.5	
Albania	10 - 15	13	3.6 - 5.3	4.5	
Austria	1.3 - 21	12	0.7 - 10	5.2	[40]
France	0.3 - 29	9.3	0.4 - 11	5.1	
	Ranges Fe (mg/kg)	**Mean Fe (mg/kg)**	**Ranges Zn (mg/kg)**	**Mean Zn (mg/kg)**	
India (Punjab)	2800.0 - 5700.0		73.0 - 320.0	-	[30]
USA	-	-	<3 - 264	43	[34]
Sweden	-	-	6 - 152	65	[33]
Japan	-	-	2.5 - 330	89	[35]
Europe	-	-	7 - 89	-	[31] [32]

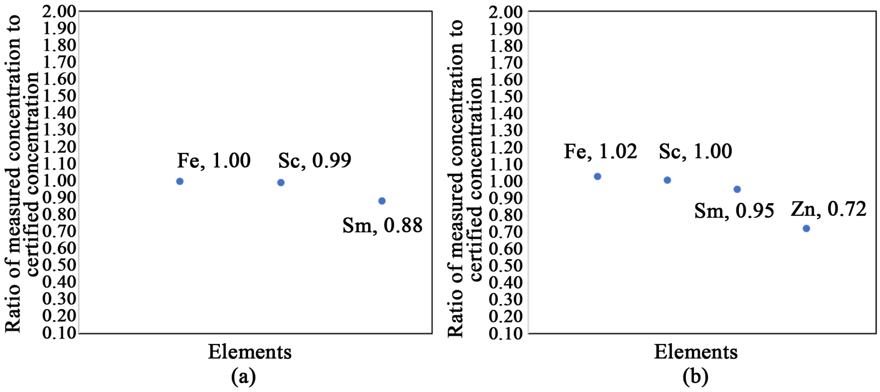

Figure S1. (a) and (b) quality control graph of the ratio of measured concentration to certified concentration of different elements by IAEA-SL-1 and CRM NIST-1633b Coal Fly Ash, respectively.