Research Article

Analyses of uranium and fluoride in diammonium phosphate fertilizers marketed in India during 2021-2022

Lokeshkumar P Ramteke[1], Raghav S Soni,[1] Babulal Rebary[2], Ashwin W Patwardhan[1]* Dilip D Sarode[1],
Pushpito K Ghosh[1]*

[1]Department of Chemical Engineering, Institute of Chemical Technology, Mumbai, India.

[2]Analytical Division, CSIR-Central Salt and Marine Chemicals Research Institute, Bhavnagar, India.

Uranium concentrations were estimated of 11 phosphate fertilizer samples collected during 2016-2019 and also of 15 Di Ammonium Phosphate (DAP) samples procured from different regions of India during 2021-2022. The samples were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), for which the quantification limit was 3 $\mu g.L^{-1}$. The reliability of the method was checked against laser fluorimetry and X-ray fluorescence analysis. The method was further validated through spiking studies. Uranium concentrations in the 2021-2022 sample collection were in the range of 8-360 mg $[U].kg^{-1}$ P_2O_5. The average uranium content was estimated to be 204.2 mg $[U].kg^{-1}$ P_2O_5, with standard deviation of 105.7 mg, which was comparable to the average of 243 mg $[U].kg^{-1}$ P_2O_5 reported for 303 phosphate fertilizer samples in a German repository. Following on from previous analyses of fluoride in phosphate fertilizers, the DAP samples collected during 2021-2022 were also analyzed for fluoride to assess the current scenario. Ion chromatography and ion selective electrode were employed for analyses, as before. Whereas a few samples contained negligible fluoride, the majority of the samples fell in the range of 20-40 g $[F].kg^{-1}$ P_2O_5, and one sample had as much as 53 g $[F].kg^{-1}$ P_2O_5. The average concentration was 24.3 g $[F].kg^{-1}$ P_2O_5, with standard deviation of 13.3 g. When compared with previous data, there was a worsening trend of fluoride contamination. No correlation was seen between uranium and fluoride concentrations. The incremental loads of uranium and fluoride in farmlands from application of DAP fertilizers were estimated to be 1,320 and 154,830 metric tonnes per annum, respectively, based on the 2020-2021 (April-March) DAP consumption figure of 11.911 million metric tonnes. Uranium and fluoride contamination emanating from application of phosphate fertilizer is a cause of concern that requires prompt remedial measures. If the uranium can be separated out and purified, it can help generate 8.8 GW of nuclear power. This is more than the present generation of 6.9 GW of nuclear power. Similarly, recovery and recycle of fluoride in desired form can cater to the entire requirement of the fluorochemicals industry.

Key words: Phosphate fertilizers, DAP, uranium, fluoride, analysis, farmland pollution

INTRODUCTION

Rock Phosphate (RP) is the primary feedstock for production of phosphate fertilizers. It is increasingly being viewed as a strategic material (Gilbert, 2009). 270 Million Metric Tonnes (MMT) of RP was mined in 2018, with China, Morocco, United States and Russia accounting for the bulk of the production (Blackwell et al., 2019). The P_2O_5 content in beneficiated rock varies from 32% to 39% w/w (Table 1) (EFMA, 2000). RP exists as fluorapatite $[Ca_{10}(PO_4)_6(F,OH)_2]$ and francolite $[Ca_{10}(PO_4)_{6-x}(CO_3)_x(F,OH)_{2+x}]$ in igneous and sedimentary deposits, respectively, the fluoride content varying in the range of 2% to 4% w/w (Van Kauwenbergh, 2010). Popular phosphate fertilizers produced from RP include: Single Super Phosphate (SSP) $[3Ca(H_2PO_4)_2 \cdot 7CaSO_4 \cdot 2H_2O]$, Triple Super Phosphate (TSP) $[Ca(H_2PO_4)_2]$ and Di Ammonium Phosphate (DAP) $[(NH_4)_2HPO_4]$. Theoretical P values as per the compositions are: 11.1%, 26.7% and 23.5%, respectively; the corresponding figures expressed in terms of P_2O_5 content are: 22.4%, 60.7% and 53.8%. SSP and TSP are obtained from the reaction of RP with H_2SO_4 (Equation (1)) and H_3PO_4 (Equation (2)), respectively, whereas DAP is obtained from the reaction of H_3PO_4 with NH_3 (Equation (3)).

*Corresponding author. Pushpito K Ghosh,
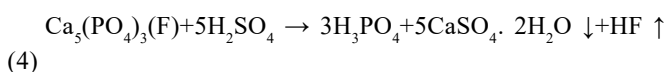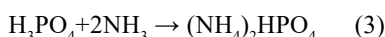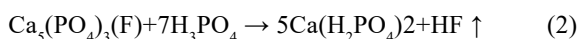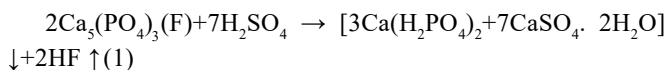E-mail: pk.ghosh@ictmumbai.edu.in.
Ashwin W Patwardhan, E-mail: aw.patwardhan@ictmumbai.edu.in.

Table 1. P_2O_5, fluoride and uranium concentrations in commercially important Rock Phosphate (RP) from different regions[a].

	Russia	Phlaborwa, S. Africa	Khouribga, Morocco	Florida, USA	Senegal
P_2O_5 (g.kg^{-1} RP)	389	368	334	343	367
F (g.kg^{-1} RP)	33	22	40	39	37
U(mg.kg^{-1} RP)[b]	9.3	113.6	156.9	85.7	105.1
[a]EFMA, 2000; [b]U values were calculated from U_3O_8 data $\{[U]=0.848[U_3O_8]\}$					

H_3PO_4 can be produced from RP by the 'thermal route' or through the reaction of Equation (4), commonly referred to as the 'wet process'. The latter process has been adopted in fertilizer production for reasons of cost-effectiveness.

$$2Ca_5(PO_4)_3(F)+7H_2SO_4 \rightarrow [3Ca(H_2PO_4)_2+7CaSO_4. \ 2H_2O]\downarrow+2HF\uparrow \quad (1)$$

$$Ca_5(PO_4)_3(F)+7H_3PO_4 \rightarrow 5Ca(H_2PO_4)2+HF\uparrow \quad (2)$$

$$H_3PO_4+2NH_3 \rightarrow (NH_4)_2HPO_4 \quad (3)$$

$$Ca_5(PO_4)_3(F)+5H_2SO_4 \rightarrow 3H_3PO_4+5CaSO_4. \ 2H_2O \downarrow+HF\uparrow \quad (4)$$

The fluoride content in RP varies in the range of 2% to 4% w/w (Table 1). Some of the fluoride is released as $HF/H_2SiF_6/SiF_4$ in the course of fertilizer and H_3PO_4 production (Eq. 1, 2, 4). The extent of separation depends on process parameters but it is never complete. Commercial processes are therefore operated to further eliminate fluoride from H_3PO_4 (Samrane, 2011). There are several reports of fluoride pollution emanating from phosphate fertilizer plants (Dartan, 2017; Dolar, 2011).

RP contains other harmful constituents also, uranium being among these. In one of the earliest studies reported, the uranium content in 316 RP samples collected from different regions of the world were analysed on a scintillation counter. The concentrations varied by more than two orders of magnitude – from 3 mg [U].kg^{-1} in Chile and Ecuador to 399 mg [U]. kg^{-1} in South Carolina, USA – the median value being 59 mg [U].kg^{-1} (Menzel, 1968). Uranium concentrations are also reported for commercially important RP sources (Table 1). The concentrations range from 9.3-156.9 mg [U].kg^{-1} (EFMA, 2000). Advanced analytical techniques such as X-ray fluorescence spectroscopy (XRF), Laser Induced Breakdown Spectroscopy (LIBS) and Low Background Counting (LBC) have been compared recently for uranium estimation in RP (Al-Eshaikh, et al., 2016). Employing high energy resolution fluorescence detected X-ray absorption near-edge structure spectroscopy (HERFD-XANES), it has been further shown that 40% to 60% of uranium in RP exists as U (IV) and the rest as U (VI) (Vogel, 2020). Phosphogypsum waste obtained in the course of phosphoric acid production from RP reportedly contains uranium [ca. 14% of the uranium coprecipitates with gypsum (Eq. 4) and the rest finds its way into the acid (Zohuri et al., 2020)] and other radioactive constituents, leading to significant pollution in the vicinity of phosphate fertilizer plants (EPA, 2015).

The problem of fluoride and uranium emanating from processing of RP is not confined to the factory premises and adjoining areas alone. These hazardous constituents can end up in fertilizers if not fully removed during the manufacturing process. Their application in agricultural fields may, in that case, spread the contaminants far and wide and cause nonpoint source pollution. It has been reported, for example, that the fluorine concentration in agricultural soils in New Zealand has increased with time. The build-up was attributed to the widespread application of phosphate fertilizer year on year (Geretharan et al., 2020). India has a large agricultural base and with the growth in population, demand for fertilizers has been rising steadily. A study of fluoride concentrations in four SSP samples, one Ammonium Nitro Phosphate sample (ANP) and two DAP samples by Ion Chromatography (IC) and Ion Selective Electrode (ISE) was conducted in 2018. It can be deduced from the data that the average concentration of fluoride was 42.7 g.kg^{-1} P_2O_5 (Ramteke et al., 2018). The figure was higher in SSP samples (53.44 g.kg^{-1} P_2O_5 on average) and lower (13.15 g.kg^{-1} P_2O_5; average of two samples) in DAP samples. Four additional DAP samples collected during 2019 revealed that the problem had remained largely unchecked, with average fluoride concentration of 19.95 g.kg^{-1} P_2O_5 (Ramteke et al., 2019).

Presence of uranium in phosphate fertilizers has also been reported by various laboratories (Roessler et al., 1979; Lal et al., 1985; Yamazaki and Geraldo, 2003; Schnug and Haneklaus, 2015; Vogel, et al., 2020). The adverse impacts arising from application of such fertilizers on water bodies and soil have also been documented (Spalding and Sackett, 1972; Kratz and Schnug, 2006; Hoyer, 2015; Cioroianu et al., 2001; Jiao et al., 2012). The analytical techniques that have been deployed for uranium analysis in fertilizers and water bodies include: Fission Track (Lal et al., 1985; Yamazaki and Geraldo, 2003), Delayed Neutron Technique (Spalding and Sackett. 1972), Gamma Spectrometric Analysis (Roessler et al., 1979; Khater, 2008), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Souza, 2016), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Vogel et al., 2020), and IC (Al-Shawi and Dahl, 1995).

Lal et al. reported over three decades ago that the uranium content in Indian phosphate fertilizers was in the range of 15.9-35.8 mg.kg^{-1}, with linear dependence on the P content of the fertilizer (Lal et al., 1985). The data were consistent with the relatively low uranium content (12 mg.kg^{-1}, on average) in Indian RP (Menzel, 1968). There is, however, paucity of recent data, even as phosphate fertilizer consumption has increased from 1.886 MMT P_2O_5 during 1984-1985 to 6.910 MMT P_2O_5 during 2018-2019 (Fertilizer Association of India, 2021), P_2O_5 consumption was reportedly 9.268 MMT [11.911 MMT of DAP (46% P_2O_5), 4.489 MMT of SSP (16% P_2O_5), and 11.811 MMT of NPKS complex fertilizer (26% P_2O_5)] during 2020-21 (April-March) (Indian Express, 2021). Indigenous production of RP,

on the other hand, has been steadily declining – it was only 1.40 million tonnes in 2019-2020 (Indian Minerals Yearbook 2020) – necessitating import of the bulk of the P_2O_5 requirement in the form of RP, phosphoric acid and finished phosphate fertilizers. Import of DAP alone was 6.1 MMT (Yao, 2020).

Given the heavy consumption of phosphate fertilizer in India and the growing dependence on imports from diverse sources, it is important to monitor commercial phosphate fertilizers not only for their nutrient values but also for the presence of hazardous constituents. Further to our previous work, we report herein new data on fluoride concentrations in fifteen new DAP samples and one MAP sample collected from various regions of India during 2021-2022. Analyses were conducted by IC and ISE methods reported previously (Ramteke et al., 2018). We also report uranium data of 27 phosphate fertilizer samples collected during 2016-2022. The first lot of samples were analysed for uranium by four different techniques [Laser Fluorimetry (LF) (Veselsky, 1988), ICP-OES (Li et al.,

2021), ICP-MS (Vogel et al., 2020), XRF analysis (Al-Eshaikh et al., 2016)]. Rest of the samples were analyzed for uranium by ICP-MS alone.

MATERIALS AND METHODS

Materials

SSP samples 1-4, DAP samples 1-6 and ANP 1, were from previous collections (Ramteke et al. 2018, 2019). DAP samples 7-21 and one monoammonium phosphate sample (MAP 1) were collected during 2021-2022. Sample details of 2021-2022 collections are provided in the Table 2. P_2O_5 and N values in the procured fertilizer samples were checked through ICP-MS and IC analyses (refer to detailed procedures under Analytical methods below). P_2O_5 and N concentrations in DAP were in the range of 49.9% to 57.9% w/w and 16.6% to 20.3% w/w against the theoretical values of 53.8% and 21.2% w/w.

Table 2. Sample details of 2021-2022 collections.

Sample code	Company	Place of procurement	Date of procurement	% P_2O_5 (w/w) [a, b]	% N (w/w) [a, b]
MAP 1	C1	Online (C1 site)	November 2021	78.5	13.1
DAP 7	C1	Pune, Maharashtra	October 2021	57.3	17.6
DAP 8	C2	Vadodara, Gujarat	November 2021	55.4	19.4
DAP 9	C3	Vadodara, Gujarat	November 2021	54.2	19.2
DAP 10	C1	Odisha	October 2021	57.9	20.3
DAP 11	C1	Raipur, Chhattisgarh	December 2021	54.6	17.6
DAP 12	C4	Raipur, Chhattisgarh	December 2021	58.0	17.5
DAP 13	C5	Raipur, Chhattisgarh	December 2021	50.7	16.8
DAP 14	C6	Raipur, Chhattisgarh	December 2021	51.9	16.9
DAP 15	C7	Latur, Maharashtra	December 2021	55.4	18.2
DAP 16	C1	24 Parganas, West Bengal	January 2022	52.0	18.4
DAP 17	C5	24 Parganas, West Bengal	January 2022	56.8	16.9
DAP 18	C8	Madurai, Tamil Nadu	January 2022	50.6	16.6
DAP 19	C9	Madurai, Tamil Nadu	January 2022	52.6	19.5
DAP 20	C1	Jharkhand	February 2022	50.0	-
DAP 21	C10	Punjab	February 2022	50.8	-

[a] Analyses of P and NH_4^+ (refer to the calibration plots in Figures S1-S6) were undertaken at 0.1 $g.L^{-1}$ DAP concentration; [b]Theoretical values of P_2O_5 for DAP and MAP are 53.8% and 61.7%, and for N the values are 21.2% and 12.2% *w/w*, respectively.

Analytical methods

SSP 1-4, DAP 1-2 and ANP 1 were analysed for uranium by ICP-OES [National Centre for Compositional Characterisation of Materials (NCCCM), Hyderabad], LF [Bhabha Atomic Research Centre (BARC), Trombay] and ICP-MS [Central Salt and Marine Chemicals Research Institute (CSMCRI), Bhavnagar; Institute of Chemical Technology (ICT), Mumbai]. SSP 2 and DAP 1 were analysed by XRF additionally. MAP 1 and DAP 7-22 were analysed by ICP-MS only. All samples for uranium analyses were sent to the respective laboratories in coded form. There was no exchange of data among the laboratories engaged in the above analyses.

Analyses of uranium by ICP-OES at NCCCM, Hyderabad: Fertilizer sample (100 mg) was dissolved in 100 mL deionised water and analysed by ICP-OES without any further dilution. Analyses were carried out using an ICP-OES (Ultima 2, Horiba Jobin-Yvon, France) equipped with a concentric nebulizer coupled to a cyclonic spray chamber. The Ultima 2 spectrometer comprises a Czerny-Turner monochromator equipped with a 2400 grooves/mm holographic grating. RF power-1100 W, Plasma gas flow-12.1 L min^{-1}, auxiliary gas flow- 0.9 L min^{-1} with a nebulizer gas flow- 0.4 L min^{-1}; wavelength of uranium: 409.014 nm.

Analyses of uranium by LF at BARC, Trombay: LF analyses were carried out with LF 003 uranium analyser. The instrument specification and other details have been previously reported (Kumar et al., 2008). ETHOS ONE high-performance microwave digestion system (Milestone, Italy) was used for sample dissolution. Milli-Q Plus water purification system (Millipore Corp., Milford, MA) was used for preparation of 18.2 MΩ water. Supra pure grade HNO_3 (65%), HF (40%) and H_3PO_4 (85%) from Merck were used for all the experiments. Samples were handled in a clean laboratory work area of class 100, designated for trace element analysis. All reusable labware were soaked in 10% v/v HNO_3 overnight, followed by rinsing with Milli-Q water and stored in 0.1% HNO_3 till further use. Each of 0.2 g samples were weighed and transferred to a heavy-duty PTFE vessel of microwave digester. 2.5 mL of HNO_3, 0.25 mL of HF and 2.5 mL of water were added into it. Vessels were packed as per protocol and subjected to microwave for dissolution as per the programme in Table S1. The samples were made up to 10 mL in perluoroalkoxy volumetric flask with ultrapure water. Each of 1 mL samples from the volumetric flask was taken in PTFE vessel and evaporated to dryness on a hot plate to remove HNO_3 and HF completely and made up to 10 mL with 5% H_3PO_4. Samples were diluted within the calibration range of the instrument and analyzed. Three blanks were also run along with the samples. Final results were blank corrected.

Analyses of uranium and phosphorus by ICP-MS at CSMCRI, Bhavnagar: ICP-MS analyses were carried out on Thermofisher, iCAP RQ single quadrupole ICP-MS analyser. The entire workflow was managed by Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software. Details of the instrument and operation can be found in the Thermofisher website (Thermo Scientific iCAP RQ ICP-MS). The calibration plot for uranium is shown in Figure S1.

The quantification limit for uranium in solution was 3 µg.L^{-1}. 50 mg samples of phosphate fertilizers were weighed. 250 µL HNO_3 and ultrapure water were added into it to a final volume of 50 mL. At this concentration (1 g.L^{-1}), the quantification limit of uranium in the fertilizers was 3 mg.kg^{-1}. Solutions were shaken well prior to analysis. The same instrument was used for phosphorus estimation after 10-fold dilution of the above solution. Calibration plot for phosphorus is given in Figure S2.

Analyses of uranium by ICP-MS at ICT, Mumbai: Some of the uranium analyses were also carried out at ICT employing the same instrument and sample preparation procedure described above for analyses by CSMCRI. The calibration plot is shown in Figure S3.

Analyses of uranium by XRF: XRF analyses of SSP 2 and DAP 1 were carried out through the assistance of ONGC Energy Centre. Analysis was conducted on the SPECTRO XEPOS energy dispersive X-ray (Pd/Co alloy anode X-ray tube) fluorescence (ED-XRF) spectrometer, SPECTRO Analytical Instruments GmbH. SSP 2 was analysed as powder and DAP 1 as pressed tablet. Measurements were made in air atmosphere, with voltage and current settings of 45.1 kV and 0.9 mA, respectively. The spectrum resolution was 132.3 eV and overall measurement time was 150 s. Absolute error was in the range of 0.4-0.5 µg.g^{-1}.

Analyses of fluoride: Fluoride analyses by IC (CSMCRI, ICT) and ISE (ICT) were carried out by the same procedures reported previously (Ramteke et al., 2018). Calibration plots for IC analyses at CSMCRI and ICT are presented in Figures S4 and S5, respectively.

Analyses of ammonium: NH_4^+ analyses were carried out at ICT on Dionex ICS 5000+ IC instrument employing Dionex IonPac™ CS16 Analytical (5 × 250 mm) column with IonPac CG16 Guard (5 × 50 mm) column; Eluent: 30 mM methanesulfonic acid; Flow Rate: 1 mL.min^{-1}; Column Temp: 40ºC; Injection Volume: 25 µL; Suppressed Conductivity Detection (Cation Self Regenerative Suppressor (CSRS 300, 4 mm); Auto suppression Recycle mode, 89 mA). The calibration plot is given in Figure S6.

RESULTS

Analyses of uranium in commercial phosphate samples

Preliminary analyses of fertilizer samples for uranium were carried out by ICP-OES at NCCCM, Hyderabad. Only four samples (SSP 3, SSP 4, ANP 1 and DAP 2) were subjected to analyses. Measurements were made at 1g.L^{-1} sample concentrations. The selected spectrum peak of 409.014 nm is reported to give the lowest interference (Li et al., 2021). Two samples gave uranium values <50 mg [U].kg^{-1} of fertilizer indicating a quantification limit of 50 µg.L^{-1} (Table 3). In view of the need for detection with greater sensitivity, experiments were conducted subsequently at BARC employing the technique of LF. Uranium absorbs strongly in the region of 260–350 nm and fluoresces in the region of 450–600 nm with quantum yield of almost unity. Uranium detection sensitivity below 3 µg.L^{-1} can be achieved through this technique (Kumar et al., 2008). Interferences due to other species were taken care of by the standard addition method and checked for recoveries

in the samples. The recoveries were within 96% to 102%. The detailed procedure is provided under Materials and Methods. Data for SSP 1-4, ANP 1 and DAP 1-2 are presented in Table 3. SSP and ANP samples, which contained 16% to 20% w/w P_2O_5 as per manufacturer specifications, gave absolute uranium concentrations in the range of 35-55 mg [U].kg^{-1} whereas the concentrations for the two DAP samples with higher (46%) P_2O_5 content were in the range of 80 - 110 mg [U].kg^{-1}. The samples were analysed next by ICP-MS (Vogel et al., 2020) at CSMCRI, Bhavnagar and the data are compiled in Table 3. ICP-MS reportedly has low tolerance towards TDS (0.2% w/v max.) (Thermo Fisher Scientific, ICP-OES/ICP-MS) and hence sample concentration was initially restricted to 0.01% (0.1 g.L^{-1}). Another set of results was generated for SSP 2 and DAP 1 in a private laboratory that used the technique of XRF to analyse the solid fertilizer samples directly (Table 3). This technique has been investigated previously for uranium analysis in phosphate rocks (Al-Eshaikh, et al., 2016) and online uranium analysis in mining and processing industries, typically with a detection limit of 30-50 mg.kg^{-1} (Hasikova et al., 2015). Advanced units such as SPECTRO XEPOS energy dispersive XRF analyser reportedly have detection sensitivity of <5 mg.kg^{-1} (Heckel et al., Spectro Analytical Instruments) As can be seen from Table 3, the LF, ICP-MS and XRF data were broadly in accord, the average of the three being 50.12 and 111.75 mg [U].kg^{-1} for SSP 2 and DAP 1, with standard deviations (σ) of 7.8 and 5.6 mg [U].kg^{-1}, respectively. All further analyses were carried out by ICP-MS only. Four commercial samples of DAP (DAP 3-DAP 6) were collected during 2019 and analysed during September to October, 2019 at CSMCRI. Analyses were carried out at 0.1 g.L^{-1} sample concentration as before. DAP 3, DAP 4 and DAP 6 showed uranium concentrations higher than those of DAP 1 and DAP 2, whereas it was below the quantification limit (30 mg [U].kg^{-1}) in DAP 5. DAP 4 and DAP 6 were analysed repeatedly (3-4 times), preparing fresh solutions each time, and the values ranged from 256.2-279.0 and 126.3-149.4 mg [U].kg^{-1} of fertilizer, respectively. The margin of error was within

± 10%. The samples were analysed once again (at ICT) after two years of storage in plastic bags. Analyses were carried out at 0.1 g.L^{-1} and 1.0 g.L^{-1} fertilizer concentrations. (Even at this higher concentration, the TDS of the solution was within the recommended TDS limit of 0.2% for ICP-MS analysis (Thermo Fisher Scientific, ICP-OES/ICP-MS)). The quantification limit was 3 mg [U].kg^{-1} at 1.0 g.L^{-1} concentration. The results are presented in Table 4. It can be seen that the trend of uranium concentrations obtained at ICT was the same as the earlier analyses at CSMCRI in 2019. Absolute values differed considerably, however, especially in the cases of DAP 3 and DAP 4. The differences were likely on account of changes in the sample during the long period of storage. Furthermore, it can be seen from the ICT data that the results were comparable at both concentration levels. The average over the four samples (DAP 3-DAP 6) was 128.3 mg [U].kg^{-1} (σ =69.8 mg [U].kg^{-1}) for the set of results obtained at 1 g.L^{-1} concentration. A spiking experiment was also conducted with DAP 4 at 1 g.L^{-1} concentration. Deviation in the reading was +3.32% (Table S2).

Table 5 presents uranium concentrations in 15 DAP samples collected during 2021-2022. All the analyses were conducted with 1 g.L^{-1} DAP solutions. Uranium concentration was lowest (4.1 mg [U].kg^{-1} DAP) in DAP 18. Uranium concentrations were also comparatively low for DAP 7, DAP 13 and DAP 21. The majority of the samples from 2021-2022 collection exhibited uranium concentrations in the range of 100-200 mg [U].kg^{-1} DAP, the maximum value of 189.3 mg [U].kg^{-1} DAP being recorded for DAP 19. The average for all 15 samples was 110.9 mg [U].kg^{-1} DAP. The standard deviation was high (σ =57.4 mg [U].kg^{-1} DAP) in view of the wide variation in concentrations – from 4.1 to 189.3 mg [U].kg^{-1} DAP. Table 5 also includes uranium concentrations on P_2O_5 basis. The average uranium concentration was 204.2 mg [U].kg^{-1} P_2O_5, with σ =105.7 mg. One sample of MAP (MAP 1), which was procured along with the 2021-2022 DAP samples, was also analysed. The uranium concentration was 3.1 mg [U].kg^{-1} MAP (4.0 mg [U].kg^{-1} P_2O_5).

Table 3. Concentration of uranium in phosphate fertilizer as estimated by four different analytical techniques.

Fertilizer sample	Uranium concentration (mg [U].kg^{-1} of fertilizer)				
	LF	ICP-OES	ICP-MS	XRF	Average of LF, ICP- MS, XRF
SSP 1	52.00 ± 2.20		43.16 ± 0.05		
SSP 2	55.00 ± 1.80		56.36 ± 0.29	39 ± 0.4	50.12 σ=7.8
SSP 3	36.00 ± 1.40	<50	56.83 ± 0.32		
SSP 4	35.00 ± 0.80	50	31.66 ± 0.79		
ANP 1	53 ± 1.50	<50	44.02 ± 0.58		
DAP 1	104 ± 4.30		114.06 ± 0.73	117.2 ± 0.5	111.75 σ=5.6
DAP 2	85 ± 3.60	50	134.40 ± 0.42		

Table 4. Uranium analyses (by ICP-MS) of DAP samples collected during 2019.

Sample name	mg [U].kg⁻¹ of fertilizer		
	0.1 g.L⁻¹ DAP solution[a,b]	0.1 g.L⁻¹ DAP solution[b,c]	1 g.L⁻¹ DAP solution [b,c]
DAP 3	200.2	151.3	166.4
DAP 4	256.2-279.0	216.3	200.1
DAP 5	BQL[d]	BQL[d]	14.9
DAP 6	126.3-149.4	125.2	131.9
Average			128.3; σ= 69.8

[a]Analyses conducted at CSMCRI, Bhavnagar during the period September 2019-Dec 2020 (refer to calibration plot in Figure S1). The samples were analysed 2-3 times during this period; [b]Quantification limit of uranium in DAP = 30 mg [U].kg⁻¹ and 3 mg [U].kg⁻¹ for 0.1 g.L⁻¹ and 1 g.L⁻¹ DAP solutions, respectively. [c]Analyses at ICT Mumbai on April 2, 2022 (refer to calibration plot in Figure S3); [d]BQL = Below quantification limit.

Table 5. Uranium concentrations in 2021-2022 DAP fertilizer collection.

Sample name	mg [U].kg⁻¹ fertilizer [a]	mg [U].kg⁻¹ P_2O_5 [b]	Sample name	mg [U].kg⁻¹ fertilizer [a]	mg [U].kg⁻¹ P_2O_5 [b]
DAP 7	57.2	99.8	DAP 15	111.0	200.2
DAP 8	180.1	324.8	DAP 16	115.6	222.1
DAP 9	178.0	328.4	DAP 17	106.1	187.0
DAP 10	162.8	280.9	DAP 18	4.1	8.2
DAP 11	151.4	277.2	DAP 19	189.3	360.1
DAP 12	111.7	192.7	DAP 20	130.0	260.0
DAP 13	16.4	32.3	DAP 21	33.6	66.1
DAP 14	116.0	223.5			
Average of all DAP samples				110.9, σ =57.4	204.2, σ =105.7

[a]Analyses conducted on ICP-MS using 1g.L⁻¹ fertilizer solution at which concentration the quantification limit of uranium was 3 mg.kg⁻¹ of fertilizer; [b]Based on the P_2O_5 data in Table 2

Analyses of fluoride in 2021-2022 phosphate fertilizer samples

The fluoride content in the DAP fertilizers (DAP 7-21) collected during 2021-2022 were also analysed. Analyses were conducted employing IC and ISE techniques. The application of these methods has been reported previously (Ramteke et al., 2018, 2019) for analyses of SSP 1-4, ANP 1 and DAP 1-6. In the present study, six of the fifteen samples (DAP 7-10, DAP 18-19) were analysed by both the methods. The results were in reasonable agreement, and exhibited similar trends (Table 6). Rest of the samples were analysed by either of the two methods:

DAP 11-17 by ISE and DAP 20 and 21 by IC. The data are summarized in Table 6. Concentrations are expressed both with respect to fertilizer weight and also per kg P_2O_5. Only three of the fifteen DAP samples had fluoride concentration ≤ 0.5 % [F] in DAP (= 8 g [F].kg⁻¹ P_2O_5). Of these, the concentration was lowest for DAP 17 (0.18%). Ten out of fifteen samples had more than 1% fluoride w/w of DAP, while DAP 16 and DAP 20 contained fluoride in excess of 2% w/w of DAP (52.9 g and 42.8 g [F].kg⁻¹ P_2O_5 in DAP 16 and DAP 20, respectively). MAP 1 was also analysed for fluoride. The concentration was below the detection limit in ISE analysis and 0.08% w/w by IC.

Table 6. Fluoride concentrations in 2021-2022 DAP fertilizer collection.

Sample name[a]	[F] (% w/w fertilizer)			g [F].kg^{-1} P$_2$O$_5$[e]
	IC[b,c]	ISE[d]	Average	Average
DAP 7	0.64[b]	0.61	0.63	11.0
DAP 8	1.06[b]	1.22	1.14	20.6
DAP 9	1.44[b]	1.28	1.36	25.1
DAP 10	1.77[b]	1.96	1.86	32.1
DAP 11	-	1.73	1.73	31.7
DAP 12	-	1.64	1.64	28.3
DAP 13	-	1.31	1.31	25.9
DAP 14	-	0.35	0.35	6.7
DAP 15	-	1.85	1.85	33.4
DAP 16	-	2.75	2.75	52.9
DAP 17	-	0.18	0.18	3.2
DAP 18	0.88[c]	0.79	0.83	16.4
DAP 19	0.52[c]	0.32	0.42	8.0
DAP 20	2.14[c]	-	2.14	42.8
DAP 21	1.37[c]	-	1.37	26.9
Average of all DAP samples			1.30 σ=0.70	24.3 σ=13.3

[a]All the analyses were undertaken at 0.1 g.L^{-1} fertilizer concentration. [b] IC analysis at ICT, Mumbai; [c]IC analysis at CSMCRI, Bhavnagar; [d]Analysis by ISE at ICT Mumbai. [e]Based on the data in Table 2.

DISCUSSION

Considering that DAP fertilizers were sourced from various parts of the Country during 2021-2022 (Table 2), Tables 6 and 7 provide realistic assessments of the extent of uranium and fluoride contamination in DAP fertilisers applied to Indian agricultural crops. Both sets of data have been compiled in graphical form in Figure 1. The average uranium concentration of 204.2 mg.kg^{-1} P$_2$O$_5$ was comparable to the average of 243 mg.kg^{-1} P$_2$O$_5$ reported previously for 303 phosphate fertilizer samples (Schnug and Haneklaus, 2015). Data pertaining to older samples going back to 2016 (Tables 3 and 4) revealed that DAP and other phosphate fertilizers with high uranium contamination have been applied in farmlands for at least seven years now. There is no mention of uranium in Indian phosphate fertilizer specifications (Bureau of Indian Standards, 2018). This is probably the case in many other countries also. Some attempts have been made, however, to specify limits: The German Commission for Soil Protection is reported to have suggested the mandatory labelling of phosphate fertilizers exceeding 20 mg [U].kg^{-1} P$_2$O$_5$ (Schnug and Haneklaus, 2015). A non-negotiable limit of 50 mg [U].kg^{-1} P$_2$O$_5$ was additionally proposed. It can be seen that the average uranium concentration in the DAP fertilizers from 2020-2021 was four times the proposed ceiling of 50 mg [U].kg^{-1} P$_2$O$_5$. Only two (DAP 13, DAP 18) out of the fifteen samples were within this limit, of which the uranium content in one (DAP 18) was low enough that it would not have required any labelling either. DAP 5 from the 2019 collection would have also fallen within this range. DAP 5 and DAP 18 were procured in different years but both were from the same company (C8). Whether these fertilizers were manufactured from low-uranium RP (Table 1) or some kind of treatment was provided is not known. In some instances there were inconsistenies in the quality of DAP sold by the same company. DAP 13 and DAP 17 were both from company C5, but whereas the uranium level in the former sample was 32.3 mg [U].kg^{-1} P$_2$O$_5$, the value was 187.0 mg [U].kg^{-1} P$_2$O$_5$ in the latter, i.e., a factor of 7 difference in the relative concentrations. Similarly, whereas all the DAP samples from company C1 showed high uranium concentrations, MAP from

the same company had negligible uranium (3.1 mg [U].kg⁻¹ MAP). Considering that Indian DAP consumption was 11.911 MMT during 2020-2021, nonpoint source uranium pollution from DAP application alone was 1,320 tonnes.annum⁻¹. Bioaccumulation of uranium in crops such as sunflower and Indian mustard would be of concern (Meng et al., 2018). Uranium presence in groundwater has also increased in many parts of the Country (Babu et al., 2008; Coyte et al., 2018; Uranium occurrence in shallow aquifers in India, 2021), but this has not been ascribed specifically to phosphate fertilizer use. If uranium is separated out from phosphoric acid prior to DAP manufacture, it can serve as feedstock for generation of 8.8 GW of nuclear power (@150 MT [U].annum⁻¹. GW⁻¹ (Strategy for growth of electricity in India, 2021) [present generation of nuclear power in India is ca. 6.9 GW (World-Nuclear Association, 2021)], besides the environmental gain that would accrue. Mature technologies exist for this purpose and 20% of the uranium demand in the US in the 1980s was met through its recovery from wet process H_3PO_4 (Steiner et al., 2020). Turning to fluoride, compared to the earlier reported data of fluoride content in DAP 1-6 (Ramteke et al., 2018, 2019) – wherein the average concentration was 17.7 g [F].kg⁻¹ P_2O_5 – a worsening trend was observed in the 2021-2022 DAP samples, with the average concentration rising to 24.3 g [F]. kg⁻¹ P_2O_5 (Table 6, Figure 1). Phosphate fertilizer specifications brought out by the Bureau of Indian Standards provide a test method for fluoride but do not specify a limit as such (Bureau of Indian Standards, 2018). The incremental fluoride load in farmlands from DAP use alone was estimated to be 1,54,830 MT.annum⁻¹. It is reported that consumption of luorite rock (CaF₂) in India was 3,24,704 MT during 2019-2020 (Indian Minerals Yearbook, 2020), amounting to fluoride equivalent of 1,58,189 MT. Thus, fluoride pollution in farmlands from DAP application is equivalent to India's entire annual requirement of fluoride for manufacture of fluorochemicals. Fluoride level in groundwater has been steadily on the rise (Ali et al., 2019). Seepage of fluoride from farmlands may be a contributing factor. Bioaccumulation of fluoride in certain crops such as tea would also be of concern (Ing et al., 2021). Commercial processes exist for treatment of phosphoric acid with reactive silica to liberate residual fluoride as H_2SiF_6 (Samrane, 2011) and also for the further conversion of H_2SiF_6 into anhydrous HF required in bulk by the fluorochemicals industry (Dahlke et al., 2016). Given that the presence of fluoride in RP is ubiquitous, some of the low-fluoride DAP fertilizers (DAP 14, DAP 17) were presumably obtained by adopting such defluoridation measures. As evident from Figure 1, the majority of the DAP fertilizers in the current study were heavily contaminated in both constituents. Thus implementation of treatment processes to affect their removal does not appear to be commonplace. The first step towards effecting a transformation would be to set standards for fluoride and uranium in Indian DAP specifications. Considering the average fluoride and uranium concentrations in DAP reported above, and assuming limits of 5 g [F].kg⁻¹ P_2O_5 and 50 mg [U].kg⁻¹ P_2O_5 are enforced, fluoride and uranium pollution can be reduced by 75%. None of the DAP fertilizers procured in 2021-2022 complied with both limits. DAP 17 was the only sample that showed a fluoride value (3.2 g [F].kg⁻¹ P_2O_5) within the above limit but its uranium concentration was

high (187.0 mg [U].kg⁻¹ P_2O_5). Conversely, DAP 18 and DAP 13 analyzed for uranium within the above limit (8.2 and 32.3 mg [U].kg⁻¹ P_2O_5, respectively) but their fluoride concentrations were high (16.4 and 25.9 g [F].kg⁻¹ P_2O_5, respectively). The published literature on fluoride and uranium separation from phosphoric acid generally focuses either on fluoride removal or uranium removal.
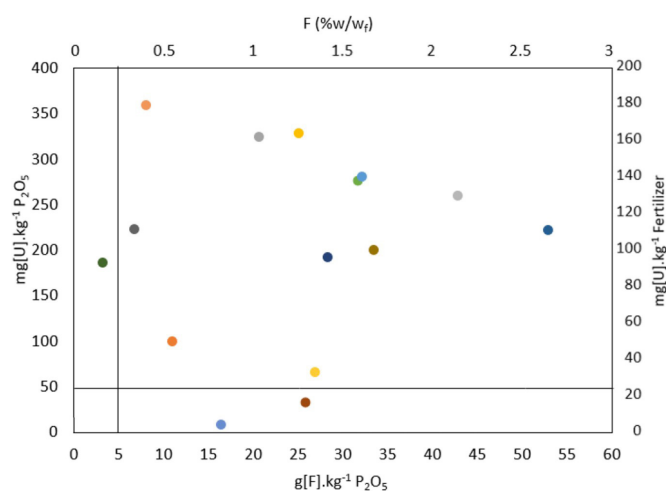

Figure 1. Mapping of uranium and fluoride concentrations in 2021-2022 DAP fertilizer samples. **Note:** (●) DAP 7, (●) DAP 8, (●) DAP 9, (●) DAP 10, (●) DAP 11, (●) DAP 12, (●) DAP 13, (●) DAP 14, (●) DAP 15, (●) DAP 16, (●) DAP 17, (●) DAP 18, (●) DAP 19, (●) DAP 20, (●) DAP 21.

There is a need to devise processes that would enable fluoride and uranium to be separated out simultaneously or sequentially from intermediate phosphoric acid when both these constituents are present in high concentrations. The separated contaminants would have potential value as feedstock after due purification and transformation to desired forms. Indeed, this must be the priority of all countries, before tapping into other resources such as fluorite for fluorochemicals and uranium ore for power generation. There is also a need to explore processes for separation of uranium and fluoride from the fertilizers given that all phosphate fertilizers are not produced through the phosphoric acid route. Development of such a technology would also be useful to deal with ammonium phosphate fertilizers such as DAP and MAP that do not conform to stipulated standards. With the above in view, laboratory experiments were performed recently to eliminate fluoride from phosphate fertilizers through a thermal treatment protocol (Ramteke et al., 2021). This was followed by removal of uranium (Ghosh et al., 2021). It remains to be seen whether the processes are amenable to scale-up.

CONCLUSION

DAP was selected for the present study in view of its commanding presence among phosphate fertilizers. Uranium and fluoride in 2021-2022 DAP samples were analysed by ICP-MS and IC/ISE, respectively, after validation studies. The two pollutants were detected in concentrations of 8–360 mg[U].kg⁻¹ P_2O_5 and 3.2–52.9 g [F]. kg⁻¹ P_2O_5, the average values being 204.2 mg and 24.3 g, respectively. Uranium and fluoride discharge in Indian farmlands from DAP application were computed to be 1,320 MT and 1,54,830 MT per year, respectively. A margin of error of ± 10% is assumed

conservatively. Actual uranium load in farmlands would be higher considering that DAP is not the only phosphate fertilizer in use. There is sizable offtake of SSP and NPK fertilizers also, and some of these fertilizers were found to be even more polluting than DAP. The most effective mitigation measure for ammonium phosphate fertilisers such as DAP is the separation of uranium and fluoride from phosphoric acid intermediate, for which well-established technologies exist already. That many of the DAP fertilizers were heavily contaminanted in fluoride and uranium indicates that these processes are not implemented by the majority of producers. Formulation of specifications for fluoride and uranium would ensure better compliance and serve as an important step towards environmental sustainability. At the same time, the treatment costs must be affordable so that fertilizer prices do not spiral out of control. Furthermore, the waste must be converted into value for a holistic solution. This would provide the necessary incentive to producers to undertake mitigation measures. Processes that remove uranium and fluoride from finished fertilizers should be developed in parallel to deal with 'off-spec' products. Studies also need to be conducted on the fate of the uranium and fluoride in farmlands. Although the current study focused on phosphate fertilisers sold in India, other nations too may be confronted with similar problems. In addition to fluoride and uranium, rock phosphate is known to contain several other harmful ingredients such as arsenic, cadmium, chromium and rare earth elements. Their presence was not investigated in the present study.

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