



Comparison of simple soil-solution extraction techniques for assessing transfer of metals from soil to plant in contaminated soils

D GOLUI¹, S P DATTA², B S DWIVEDI³ and M C MEENA⁴

ICAR-Indian Agricultural Research Institute, New Delhi 110 012

Received: 28 March 2018; Accepted: 3 April 2018

ABSTRACT

An attempt was made to evaluate simple techniques for extraction of soil solution for predicting uptake of Zn, Cu, Ni, Pb and Cd by spinach (*Beta vulgaris* L. var. All Green) grown on metal contaminated soils under modelling framework. Twenty-eight surface soil samples (0-15 cm) with heterogeneous chemical properties were collected. A pot experiment was conducted using spinach as a test crop. The leachate from experimental pots was collected with the help of plastic container installed below the pots. The 1:2 and 1:5 soil: water ratio was used for soil solution extraction. The total concentration of Zn, Cu, Ni, Pb, and Cd in soil solution was determined using ICP-MS. Harvested plant sample was analyzed for total Zn, Cu, Ni, Pb, and Cd using ICP-MS. For predicting metal uptake by spinach free ion activity model (FIAM) was used and total metal concentration in soil solution was used as an input of FIAM. Higher concentration of all metal in 1:5 soil-water ratio were recorded than that in 1:2 soil-water ratio. The free ion activity model as a function of total metal concentration in soil solution, as measured by 1:5 soil: water extraction, could explain the variability in metal content in spinach to the extent of 94% for Zn, 67% for Cu, 80% for Ni, 50% for Pb and 75% for Cd, respectively. Extraction of soil with 1:5 soil-water ratio is more efficient and suitable for predicting metal uptake by spinach as compared to that of 1:2 and leachate extraction.

Key words: Bioavailability, Leachate, Metal, Soil solution, Soil water extract

Build-up of metals in soil from various sources, viz. natural, groundwater, sewage and industrial effluents as well as solid wastes is of great concern due to transfer of potentially trace toxic metals to human food-chain (Datta *et al.* 2000, Rattan *et al.* 2005, Rang Zan *et al.* 2013, Meena *et al.* 2016). In most of the studies related to assessing bioavailability of metals, the metals present in soil solids are measured along with those in solution phase. The metals present in solution phase are not measured separately (Francois *et al.* 2004). In most countries, regulatory bodies use total metal content in soil as a measure of hazard in polluted soils. But total metal content in soil is neither an indicator of intensity factor, nor represents labile fraction that affects the bioavailability of metal in polluted soils. This has been reflected in a poor relationship between the total metal content in soil and their uptake by plants (Francois *et al.* 2004, Datta and Young 2005). Simultaneously, attempts were made to relate the toxic effect of metals to some operationally defined extractable metals (Quevauviller 1998). In spite of all advancements in assessing bioavailability of metal to plants as well ecotoxicity in polluted soils, it has been well established that intensity of metals in soil solution

is of utmost importance. In this regard, extraction of representative soil solution has been a main constraint. Various procedures and techniques have been reported in the literature for the removal of soil pore water, which include squeezing of moist soil, centrifugation and *Rhizon* sampling technique (Datta and Young 2005). However, extraction of soil solution, followed by chemical analysis, and speciation using appropriate ion speciation models to determine intensity of metals in soil solution are tedious, costly and require specialized instrumentation and lab wares. Simpler techniques like soil-water extracts (1:1 and 1:5) have been developed for extraction of soil solution by US Soil Salinity Staff (1954) to characterize the salt-affected soils. Collection of leachate in the field experiment has been used in characterizing soil salinity (Yao *et al.* 2008). These techniques had been seldom used in ecotoxicity studies related to metals in soil due to poor analytical capabilities. In recent years, detection of abysmally low concentration of metals in soil solution has been made possible due to use of highly sophisticated instruments like AAS and ICP-MS/OES/AES.

The contribution of metals present in soil solution phase to plant uptake is attributed to the ability of metal intensity in solution to buffer the free metal ion at the root surface (Antunes *et al.* 2006). Several researchers reported a strong relationship between metal adsorption at the plant root surface and metal present in the soil solution (intensity).

¹Scientist, ²Professor and Principal Scientist(e mail: profssac2017@gmail.com), ³Head and Principal Scientist, ⁴Senior Scientist, Division of Soil science and Agricultural Chemistry.

Therefore, it is thought proper to evaluate the efficacy of simple soil solution extraction techniques for assessing intensity of metals in soil solution. Free ion activity model predicting transfer of metal from soil to plant based on free ion activity of metals in soil solution (Datta and Young, 2005), where soil solution was extracted using *Rhizon* sampler technique and centrifugation. Hence, it would be worthwhile to assess how far soil water extract represent *in-situ* soil solution in respect of intensity of metal under modelling framework (FIAM) for routine risk assessment of metal polluted soils.

Hence, the present investigation was undertaken with the objective: to compare the concentration of metals in soil-water extract and leachate as an indicator of phytoavailability using free ion activity model (FIAM).

MATERIALS AND METHODS

Twenty eight bulk surface soil samples (about 25 kg at each site) from 0-15 cm depth were collected from various locations, which have history of receiving sewage, sludge, polluted river water and industrial effluents or municipal solid waste for long time as mentioned in Table 1.

Processed soil samples were used to determine soil pH (soil :water suspension 1:2, Datta *et al.* 1997), oxidizable organic carbon (wet digestion, Walkley and Black 1934) and texture (hydrometer method, Bouyoucos 1962). Total metal content of the soil was determined by ICP-MS following the digestion with aqua regia (75% conc. HCl + 25% HNO₃) (Quevauviller 1998). All the soil samples were analyzed in triplicate. For extraction of metals, 1:2 and 1:5 soil: water ratio was followed (United States Salinity Laboratory Staff 1954). Desired soil-water mixture, in a capped plastic bottle, was placed on a mechanical shaker

for 15 minutes, allowed to stand for 1 h, and shaken again for 5 minutes. The content was filtered through Whatman No 42 filter paper and the clear leachate was analyzed for Zn, Cu, Ni, Pb and Cd using ICP-MS.

Three replicates of 4 kg capacity pots were filled with processed soil (air dried, ground and passed through a 2 mm sieve) from each site. Appropriate holes were made below the plastic pots to collect sufficient amount of leachate during the plant growth. Filled pots were used to grow spinach (*Beta vulgaris* L. var. All Green). A basal dose of N, P₂O₅ and K₂O at 11.1, 11.1 and 22.2 mg/kg soil was added as solutions to each pot through urea, diammonium phosphate and muriate of potash, respectively. Soil moisture in the pot was maintained at field capacity for one month. About 10-12 seeds of spinach were sown in each pot and a uniform plant population of 8 plants per pot was maintained after a fortnight of germination. Pots were irrigated daily with required amount of water so as to maintain the field capacity. Above ground biomass were harvested at 42 days after sowing and analyzed for total metal content. Digestion of dried sample was carried out with Suprapure HNO₃ using microwave digester and analysed for Zn, Cu, Ni, Pb and Cd using ICP-MS. For quality control, standard metal solution (Zn, Cu, Ni, Pb and Cd) was used to calibrate the ICP-MS. These standards were also included as sample in every batch of 30 samples to ensure the accuracy of analysis.

For leachate collection, each pot was put on a plastic container at 21 days of sowing and pots were irrigated. Plastic container was removed at 25 days of sowing and leachate accumulated in pot was filtered through Whatman No 42 filter paper and acidified with 0.01 M HNO₃. Concentration of Zn, Cu, Ni, Pb and Cd in the leachate was determined using ICP-MS.

Table 1 Location and description of experimental soils

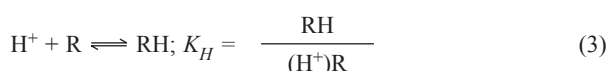
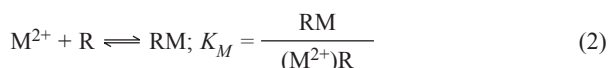
Location	No. of samples	Description
Debari, Udaipur, Rajasthan, India	9	Eight soil samples were collected from agricultural lands, which have been receiving irrigation through industrial effluents emanating from zinc-smelter plants of the Hindustan Zinc Limited, Debari, Udaipur, Rajasthan for the last fifty years. One soil sample was collected from the adjacent agricultural land, which is receiving irrigation through tube-well water for comparison.
Sonepat, Haryana, India	4	Four soil samples were collected from the fields adjoining the Atlas Cycle factory, Sonepat, Haryana, which had a history of receiving irrigation through industrial effluents for fifteen years.
Dhapa, Kolkata, West Bengal, India	3	Three soil samples were collected from landfill sites (agricultural land), where the solid wastes of the city of Kolkata have been dumped for more than forty years.
Keshopur, New Delhi, India	7	Seven samples were collected from the sewage effluent irrigated fields at Bakarwala village, west Delhi, which has been receiving irrigation through sewage effluents for the last thirty eight years under Keshopur Effluent Irrigation Scheme (KEIS) of the Delhi Government.
Madanpur khadar, New Delhi, India	3	Two soil samples were collected from river bank of Yamuna, which are irrigated with polluted river water. One surface soil sample was collected from the adjacent agricultural lands on the bank of river Yamuna which are not accessible to flood-water from Yamuna.
IARI farm, New Delhi, India	2	One soil sample was collected from sewage effluent-irrigated field of IARI farm, receiving domestic sewage water irrigation for the past fifty years. One soil sample was collected from the adjacent tube-well irrigated areas under intensive cropping.

Concept of free ion in metal pollution studies came into existence in 1970's, when scientist demonstrated that free ion activity was better predictor of metal toxicity than the total dissolved metals (Parker *et al.* 1995). This gave rise to the free ion activity model, which is based on a general chemical equilibria principle accounting interaction between the metals and sorption sites on roots (Campbell 1995). Metal present in soil solution, as measured by soil water extraction and leaching was used as an input of FIAM model. In fact, experimental evidences suggest that different solution species, viz. hydrolytic ion pair, ion complex and free ionic species remain in equilibrium with each other (Lindsay 1979). The model can be formulated as follows:

$$R_T = RH + RM + R \tag{1}$$

where, total, protonated, metal bound and free sites are represented by R_T , RH , RM and R , respectively.

Reaction of sorption sites on roots for metal ions and protons may be described by Eqs. 2 and 3:



Combining equations 1 to 3, and metal uptake by spinach can be given by:

$$M_{\text{spinach}} = \frac{K_T R_T K_M (M^{2+})}{1 + K_M (M^{2+}) + K_H (H^+)} \tag{4}$$

where, K_T = constant which express the assumption that metal uptake by spinach reflect the adsorbed metal ion on spinach root during the entire growth period, K_M and K_H = simple reaction constants, R_T = Total binding sites at root surface.

Equation 4 was used in "SOLVER" (Windows 10, USA) for parameterization of this model:

$$M_{\text{spinach}} = \frac{\text{POWER}(10, K_M * N_s) * (M^{2+})}{(1 + \text{POWER}(10, K_M * (M^{2+})) + (\text{POWER}(10, K_H) * (\text{POWER}(10, -pH)))}$$

where, N_s accounts for competition between numbers of cations for hypothetical sorption sites on root.

RESULTS AND DISCUSSION

Soil pH and EC in experimental soils were ranged from 6.43 to 8.36 and 0.41 to 6.91 dS/m, respectively (Table 2). The Walkley and Black carbon was ranged from 0.47 to 2.97%. The clay content across the soils was ranged from 9.80 to 43.8 with the average value of 22.2 %. Six textural classes namely, clay, sandy clay loam, loam, clay loam, silty clay loam and sandy loam were observed across the experimental soils.

The total content of Zn, Cu, Ni, Pb and Cd throughout the studied soils were ranged from 54.1 to 28662, 29.0 to 2305, 17.0 to 1513, 9.90 to 3793 and 0.22 to 352 mg/kg, respectively (Table 3). High values of Zn, Pb and Cd as recorded in Debari soil is due to long term application of zinc smelter effluents (Ray *et al.* 2017). Extraordinarily high values of Zn, Ni and Cd were also recorded in the soils collected from Sonepat, which had been receiving effluents from the ATLAS Cycle Factory. Higher level of Ni in the Sonepat soil can be attributed to the fact that Ni is commonly used for the production of Ni alloys with high temperature and corrosion resistance (Cempel and Nikel, 2006, Rang Zan *et al.* 2013). Higher values of total Zn and Pb were recorded in the Dhapa soils, which have been receiving municipal solid wastes and located just adjoining the roadways. Unleaded gasoline emissions from automobiles and high traffic volume on roadways in the vicinity of the Dhapa area might have role in contributing to the elevated level of Pb in the Dhapa soil (USEPA 2017). Although, higher values of Zn, Cu, and Ni were observed in Keshopur and Madanpur, the extent of accumulation of Zn, Cu, Ni, Pb and Cd was lower as compared to that in

Table 2 Physiochemical properties of experimental soils

Location	No. of soil samples	pH	EC (dS/m)	WBC (%)	Clay (%)	Textural Class
Debari	9	7.68-8.20 (7.94)	0.14-6.91 (2.32)	0.89-2.48 (1.54)	19.5-43.8 (25.0)	Sandy clay loam(4), Sandy loam (2), Clay (1), Loam (1), Clay loam(1)
Sonepat	4	7.17-7.68 (7.60)	0.37-1.36 (0.80)	0.89-1.36 (1.02)	9.80-18.8 (14.1)	Sandy loam (2), Loam (2)
Dhapa	3	6.43-7.18 (6.86)	0.36-0.86 (0.67)	2.11-2.97 (2.68)	19.8-21.8 (20.8)	Loam(3)
Keshopur	7	6.51-7.98 (7.46)	0.57-2.34 (1.14)	0.68-1.24 (0.85)	15.8-27.8 (20.3)	Sandy clay loam(3), Sandy loam (4)
Madanpur Khadar	3	7.53-7.88 (7.74)	0.43-1.40 (0.89)	0.52-1.00 (0.74)	21.8-35.8 (28.5)	Loam (1), Silty clay loam (2)
IARI	2	6.86-8.36 (7.62)	0.17-0.73 (0.45)	0.47-0.79 (0.63)	22.6-25.9 (24.3)	Sandy clay loam(2)
Overall	28	6.43-8.36 (7.61)	0.14-6.91 (1.34)	0.47-2.97 (1.27)	9.80-43.8 (22.2)	-

Data are presented in terms of range along with mean values in parenthesis.

Table 3 Total (aqua regia-extractable) metal contents in experimental soils

Location	No. of samples	Total metal content (mg/kg)				
		Zn	Cu	Ni	Pb	Cd
Debari	9	87.5-28662 (6132)	42.2-448 (138)	21.2-48.1 (30.5)	14.0-3793 (651)	0.98-352 (96.8)
Sonepat	4	905-3727 (2353)	299-2305 (1192)	291-1513 (864)	85.5-198 (133)	2.33-15.1 (9.81)
Dhapa	3	909-1305 (1069)	218-253 (239)	29.1-39.6 (34.7)	412-1145 (666)	1.48-2.13 (1.78)
Keshopur	7	54.1-381 (147)	157-293 (235)	17.0-30.0 (21.9)	9.90-25.0 (14.5)	0.22-2.51 (1.45)
Madanpur Khadar	3	65.7-171 (127)	193-353 (270)	20.0-29.0 (24.9)	11.9-21.9 (17.0)	0.55-1.26 (0.92)
IARI	2	59.9-164 (112)	29.0-37.4 (33.2)	18.7-24.0 (21.4)	11.8-14.6 (13.2)	0.53-0.87 (0.70)
Overall	28	54.1-28662 (2479)	29.0-2305 (330)	17.0-1513 (146)	9.90-3793 (305)	0.22-352 (33.2)

Data are presented in terms of range along with mean values in parenthesis.

industrial effluent-irrigated and solid waste-deposited soils. By and large, lower level of Zn and Cd were recorded in IARI soils.

Metal concentrations in soil solution as extracted with soil water extract and leachate in pot experiment is presented in Table 4. Concentrations of Zn, Cu, Ni, Pb and Cd in leachate sample as collected from pot experiment under spinach were ranged from 43.9 to 471, 39.4 to 2187, 38.1 to 854, 1.27 to 10.8 and 0.10 to 272 µg/L, respectively. Concentrations of Zn, Cu, Ni, Pb and Cd in 1:2 soil water extract were ranged from 0.49 to 389, 4.13 to 1362, 33.5 to 195, 0.15 to 34.8 and 0.05 to 123 µg/L, respectively, while total metal concentration in 1:5 soil: water extract were ranged from 1.62 to 541 for Zn, 19.1 to 374 for Cu, 21.0 to 287 for Ni, 0.07 to 25.8 for Pb and 0.05 to 332 µg/L for Cd, respectively.

It is difficult to explain the higher extraction of metal in 1:5 soil-water ratio than that in 1:2 soil-water ratio. One possible reason may be an initial lower concentration of metal in 1:5 soil water extract than that in 1:2 soil water extract, which might have encouraged the higher release of metal following steep gradient from solid to solution phase. Wider soil to water ratio (1:5) might have also led to more dissolution of other solid phases like Fe, Al-oxides and Ca, Mg- carbonate in contaminated soil compared to that in the narrower soil to water ratio (1:2). Such dissolution of solid phases might have been responsible for releasing a higher amount of metals in solution. Another reason one can envisage is that there is always higher possibility of precipitation in the narrower soil to water (1:2) compared to the wider soil to water (1:5). One may argue that if precipitation is the reason, why does the final metal concentration in 1:5 soil-water ratio is higher than that in

1:2 soil-water ratio. This can be explained based on the fact that precipitation always encourages further precipitation (Mendham *et al.* 2000). However, for arriving at concrete conclusion, soil water extraction may be done with further graded levels of soil-water ratios (1:2, 1:3, 1:4, 1:5 and 1:6) to see if the reasons as explained above are valid.

Content of metals in the above-ground biomass of spinach showed considerable variation among the experimental soils. Total Zn, Cu, Ni, Pb and Cd in spinach ranged from 57.2 to 1245, 3.85 to 40.2, 0.55 to 15.5, 0.40 to 82.0 and 0.15 to 48.3 mg kg⁻¹, respectively (Table 5).

Metal concentration as obtained from leachate, 1:2 and 1:5 soil-water extract were used for prediction of metal uptake by spinach under modelling framework (Table 6). The free ion activity model as a function of metal concentration in soil solution, as measured by 1:5 soil: water extraction, could explain the variability in metal content in spinach to the extent of 94% for Zn, 67% for Cu, 80% for Ni, 50% for Pb and 75% for Cd, respectively. The free ion activity could be accounted for as high as 49, 38, 12, 34 and 37% variation in Zn, Cu, Ni, Pb and Cd content, respectively, when total metal concentration in solution, as measured by 1:2 soil: water extraction, was used as an input. While

Table 5 Total metal content (mg/kg) in spinach

Metal	Range	Mean
Zn	57.2-1245	252
Cu	3.85-40.2	12.9
Ni	0.55-15.5	2.76
Pb	0.40-82.0	10.0
Cd	0.15-48.3	4.97

Table 4 Metal concentrations (µg/L) in soil solution for 28 experimental soils

Techniques used for soil solution extraction	Zn	Cu	Ni	Pb	Cd
Leachate (Spinach)	43.9-471 (157)	39.4- 2187 (507)	38.1-854 (174)	1.27-10.8 (3.09)	0.10-272 (12.6)
1:2:: soil: water extract	0.49-389 (28.9)	4.13-1362 (29.8)	33.5-195 (113)	0.15-34.8 (2.54)	0.05-123 (7.78)
1:5:: soil: water extract	1.62-541 (55.6)	19.1-374 (80.5)	21.0- 287 (159)	0.77-25.8 (6.66)	0.05-332 (19.4)

Data are presented in terms of range along with mean values in parenthesis.

Table 6 Model parameters for predicting uptake of Zn, Cu, Ni, Pb and Cd by spinach as a function of free metal ion activity and soil pH

Metal	Total metal concentration in leachate				Total metal concentration in 1:2 soil water extract				Total metal concentration in 1:5 soil: water extract			
	Model parameters			R ²	Model parameters			R ²	Model parameters			R ²
	K _M	* Ns	K _H		K _M	* Ns	K _H		K _M	* Ns	K _H	
Zn	0.25	-0.84	-4.33	0.46	1.67	0.25	-1.43	0.49	0.29	0.98	-2.98	0.94
Cu	-1.09	0.50	-2.47	0.23	0.01	1.01	-1.49	0.38	-1.34	1.01	-3.14	0.67
Ni	-1.74	0.25	-3.97	0.44	-1.60	0.53	-9.88	0.12	-1.41	1.07	-8.78	0.80
Pb	0.99	0.25	-0.30	0.01	0.45	8.15	-1.15	0.34	0.08	8.03	-6.85	0.50
Cd	0.20	0.25	-1.37	0.33	0.71	0.50	-0.95	0.37	0.31	1.00	-1.35	0.75

model based on leachate extract could explain as high as 46, 23, 44, 1 and 33% variability in Zn, Cu, Ni, Pb and Cd content in spinach, respectively.

Extraction of soil with 1:5 soil-water ratio is more efficient and suitable for predicting metal uptake by spinach as compared to that of 1:2 and leachate extraction. One can envisage that extraction of soil with the wider soil-water ratio (1:5) can represent better the composition of the in-situ soil solution. Because intensity of metal is affected to a lesser extent due to several chemical processes like precipitation as compared to that in narrower soil-water ratio. Datta and Young (2005) reported that the total metal present in soil solution and free ion activity of metal were almost equally effective in predicting the uptake of Zn, Cu and Cd by plant across the methods of soil solution extraction. In addition, metal ion absorption by plant roots is not fully dependent on free ion activity of metal in soil pore water (Smolders and McLaughlin, 1996; Collins *et al.* 2001). Soil water extraction technique (soil-water::1:5) is distinctly superior than other two techniques (soil-water::1:2 and leachate) for assessing intensity of metals in solution phase and subsequent prediction of metal transfer from soil to plant. This simple soil solution extraction techniques shows promise to be used in routine risk assessment of metal polluted soils.

ACKNOWLEDGEMENT

The author acknowledges the fellowship received from ICAR, New Delhi, India to undertake this research work as part of his Ph D degree.

REFERENCES

- Antunes P M C, Berkelaar E J, Boyle D, Hale B A, Hendershot W and Voigt A. 2006. The biotic ligand model for plants and metals: technical challenges for field application. *Environmental Toxicology and Chemistry* **25**: 875–82.
- Bouyoucos G J. 1962. Hydrometer method improved for making particle size analysis of soils. *Journal of Agronomy* **54**: 464–5.
- Campbell P G C. 1995. Interaction between trace metals and aquatic organisms: A critique of the free-ion activity model. (In) *Metal Speciation and Bioavailability in Aquatic Systems*, pp 45–102. Tessier A and Turner D R (Eds). John Wiley and Sons Ltd,
- Cempel M and Nikel G. 2006. Nickel, A review of its sources and Environmental Toxicology. *Polish Journal of Environmental Studies* **15**: 375–82.
- Collins R N, Onisko B C, McLaughlin M J and Merrington G. 2001. Determination of metal-EDTA complexes in soil solution and plant xylem by ion chromatography-electrospray mass spectrometry. *Environmental Science & Technology* **35**: 2589–93.
- Datta S P, Subba Rao A and Ganeshamurthy A N. 1997. Effect of electrolytes coupled with variable stirring on soil pH. *Journal of the Indian Society of Soil Science* **45**: 185–7.
- Datta S P and Young S D. 2005. Predicting metal uptake and risk to human food chain from leafy vegetables grown on soils amended by long-term application of sewage sludge. *Water, Air and Soil Pollution* **163**: 119–36.
- Datta S P, Biswas D R, Saharan N, Ghosh S K, Rattan R K. 2000. Effect of long-term application of sewage effluents on organic carbon, bioavailable phosphorus, potassium and heavy metals status of soils and uptake of heavy metals by crops. *Journal of the Indian Society of Soil Science* **48**: 836–9.
- Francois M, Dubourguier H C, Li D and Douay F. 2004. Prediction of heavy metal solubility in agricultural topsoils around two smelters by the physico-chemical parameters of the soils. *Aquatic Sciences* **66**: 78–85.
- Lindsay W L and Norvell W A. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Science Society of America Journal* **42**: 421–8.
- Meena R, Datta S P, Golui D, Dwivedi B S and Meena M C. 2016. Long term impact of sewage irrigation on soil properties and assessing risk in relation to transfer of metals to human food chain. *Environmental Science and Pollution Research* **23**: 14269–83.
- Mendham J, Denney R C, Barends J D and Thomas M. 2000. *Vogel's Textbook of Quantitative Chemical Analysis*, 6th Edition, Pearson Education Ltd, India.
- Parker D R, Chaney R L and Norvell W A. 1995. Chemical equilibrium models: Applications to plant nutrition research. (In) *Chemical Equilibrium and Reaction Models*. Loeppert R H, Schwab A P and S Goldberg. (Eds). pp 163–200. Special Publication 42. Soil Science Society of America, Madison, WI, USA.
- Quevauviller P H. 1998. Operationally defined extraction procedures for soil and sediment analysis. *Trends in Analytical Chemistry* **17**: 289–98.

- Rang Zan N, Datta S P, Rattan R K, Dwivedi B S and Meena M C. 2013. Prediction of the solubility of zinc, copper, nickel, cadmium, and lead in metal-contaminated soils. *Environmental Monitoring and Assessment* **185**: 10015–25.
- Rattan R K, Datta S P, Chhonkar P K, Suribabu K and Singh A K. 2005. Long term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater-a case study. *Agriculture Ecosystem and Environment* **109**: 310–22.
- Ray P, Datta S P and Dwivedi B S. 2017. Long-term irrigation with zinc smelter effluent affects important soil properties and heavy metal content in food crops and soil in Rajasthan, India. *Soil Science and Plant Nutrition* DOI:10.1080/00380768.2017.1404424.
- Smolders E and McLaughlin M J. 1996. Chloride increases cadmium uptake in Swiss chard in a resin-buffered nutrient solution. *Soil Science Society of America Journal* **60**: 1443–7.
- United States Salinity Laboratory Staff. 1954. Diagnosis and Improvement of Saline and Alkali Soils: 1954., Agriculture Handbook No. 60.
- USEPA. 2017. Sources of lead in soil: a literature review. Battelle Memorial Institute, Washington.
- Walkley A and Black I A. 1934. An examination of the degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Science* **37**: 29–38.
- Yao H Y, Chung S R, Ho S B and Chang Y C A. 2008. Adapting the pour-through medium extraction method to phalaenopsis grown in sphagnum moss. *Horticultural Science* **43**: 2167–70.