Rubber Science, **29**(2): 168-177, 2016 *RESEARCH ARTICLE*

QUALITY ASSESSMENT OF SOME COMMERCIAL ORGANIC AND INORGANIC FERTILIZERS MARKETED IN KERALA WITH SPECIAL REFERENCE TO HEAVY METALS

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Received: 04 April 2016 Accepted: 25 July 2016

Prasannakumari, P., Jessy, M. D. and Jacob, J. (2016). Quality assessment of some commercial organic and inorganic fertilizers marketed in Kerala with special reference to heavy metals. *Rubber Science*, **29**(2): 168-177.

Composite samples of twenty three organic fertilizers/manures were collected from the market and analyzed for moisture content, pH, electrical conductivity, total organic carbon, C: N ratio, total nutrients and heavy metals and the data were compared with quality control guidelines for city compost as per Fertilizer Control Order, 1985. It was observed that the extent of compliance varied widely with respect to different parameters. High nutrient contents, especially nitrogen, were observed in majority of the samples indicating possible adulteration with chemical fertilizers. Chromium content was very high in about 50 per cent of the tested samples. Lead content was above the toxic limit in four per cent of the samples. Cadmium, copper and zinc contents were within the permissible limits in all the samples. All the samples contained very high levels of iron. During the analysis of the samples by acid digestion, varying amounts of sand or powdered rock were left as residue, indicating mixing with such materials, possibly again as adulterants. The study clearly points to the need for establishing quality control parameters for organic fertilizers, and regulating the quality of various products marketed as organic fertilizers. Proper labeling of these fertilizers should be an immediate priority. Phosphorus fertilizers and other inorganic fertilizers commonly used in Kerala were also tested for their heavy metal contents what about lead, cadmium and zinc were within the limits specified by Food and Agriculture Organization/World Health Organization.

Keywords: Fertilizer, Heavy metals, Organic manure, Quality assessment

INTRODUCTION

Recently, there has been increasing concern regarding the environmental problems related to fertilizers, as they can be a non-point source of pollution in soils and waters. This has led to the rapid growth of the organic farming sector, where alternate source of nutrients can be availed. This move is so strong that majority of the states in India are in the process of becoming fully organic in the field of agriculture. There is a strong move to make Kerala also a fully organic-agriculture state. Gadgil/Kasturirangan reports on Western Ghats which will cover almost one-third of Kerala's geographic area also encourage organic farming (Gadgil, 2013; Kasturirangan, 2013).

Increasing interest in organic agriculture has led to the exploration of various types of

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organic wastes as possible sources of plant nutrients. As the availability of traditional organic manures such as farm yard manure is limited, farmers interested in organic farming have to depend on commercially available organic fertilizers in the market. Use of organic wastes as fertilizer has the obvious advantage of reducing the use of chemical fertilizers, apart from putting such wastes into a useful purpose. Application of organic waste to soil provides nutrients, increases soil organic matter content, improves soil structure, and enhances nutrient absorption by plants (Alloway, 1995; Singh and Agrawal, 2008). However, there is a growing concern about the authenticity of the variety of products sold in the market, as these are not labeled with quality standards

Accumulation of heavy metals in agricultural soils is of increasing concern due to its potential health risks as well as its detrimental effects on soil ecosystems (Nagajyothi *et al.*, 2010). There are many reports of the presence of heavy metals in commercial organic and inorganic fertilizers (Singh, 1991; Singh, 1994; Boss and Bhattacharya, 2008; Bolan *et al.*, 2004). Phosphorus fertilizers contain small amounts of heavy metal contaminants, especially cadmium, which are minor constituents of phosphate rock (Chien *et al.*, 2011; Javied *et al.*, 2009).

Animal dung, municipal solid waste, industrial byproducts and sludge are the most common organic wastes applied as fertilizers, either in their raw or composted forms. The fertilizer materials prepared from different organic wastes will differ in their quality depending on the raw material. Quality standards and regulations for marketing of organic fertilizers are not well established as in the case of mineral fertilizers in India. As per the standards of organic farming, organic fertilizer includes biodegradable materials of microbial, plant or animal origin, *e.g*, compost, vermicompost, biofertilizers *etc*. The ministry of Agriculture, Government of India has included four biofertilizers (*Rhizobium, Azotobacter, Azospirillum* and P-solubilizers, mycorrhizal biofertilizer, potassium mobilizing biofertilizer, zinc mobilizing biofertilizer) under Fertilizer Control Order, 1985 to make legal control on quality of biofertilizers (FAI, 2007). Simultaneously, manures such as city compost, vermicompost, phosphate rich organic manure (PROM), and non-edible de-oiled cake fertilizers have also been included in Fertilizer Control Order (FCO), 1985 for their regulatory control.

There are many rubber growers who also adopt organic farming even as rubber growing soils are rich in organic carbon content and the chemical fertilizer requirement is less in rubber compared to many other crops (Karthikakuttyamma *et al.*, 2000). The present study was carried out to evaluate the quality of different organic fertilizers/manures marketed in Kerala, in terms of their physico-chemical properties, nutrient availability and heavy metal contents. In continuation with this, commonly used chemical fertilizers were also analyzed for their heavy metal contents.

MATERIALS AND METHODS

Composite samples of twenty three different organic fertilizers/manures were collected from their dealers at different places during September-October 2013. The samples were collected following the methods of US-EPA part 503 rule (composite sample of several grab samples combined) (US-EPA, 1995). These samples include biocomposts, city composts and products based on industrial wastes and animal manure. Obviously these samples do not cover all such fertilizers sold or available in Kerala. Keeping

up with accepted professional ethics, the identities of the organic fertilizers are kept confidential. Samples of chemical fertilizers were collected from authorized dealers, following the method of FAI (2007).

Moisture content of the organic fertilizer/manure samples was estimated by gravimetric method by measuring loss of weight at 70 °C. The samples were dried at 70 °C, sieved through two mm sieve and ground before analyzing the chemical contents. pH and electrical conductivity (EC) were measured in the slurry of the dried sample (sample : water ratio of 1 : 5). Volatile solids (VS) were determined as weight loss during dry combustion at 550 °C for 5 hours in muffle furnace. Total organic carbon was estimated as % C = % VS/1.8 (Singh, 2004). Total nitrogen in the samples was estimated by Kjeldahl's method after decomposing the samples in con. H_2SO_4 (Bremner and Mulvaney, 1982). Total phosphorus (P) was determined by digesting the sample in diacid mixture (H_2SO_4: $HClO_4$ in 1:1 ratio), and P in the digest was measured by spectrophotometric technique using the vanadomolybdate yellow color method (Olsen and Sommers, 1982). Potassium was determined by flame photometry after dry ashing the samples in a muffle furnace at 550 °C, followed by digestion in con. HCl (FAI, 2007).

Heavy metal contents in organic and inorganic fertilizers were determined after digestion with triacid mixture (HNO_3, H_2SO_4 and $HClO_4$ in the ratio 10:1:4) and subsequent measurement of elemental concentration by atomic absorption spectrophotometry. Other physico-chemical parameters of chemical fertilizers were not attempted in the study as these are already certified products. The physico-chemical parameters of organic fertilizers were compared with quality control guidelines of city compost as per Fertilizer Control Order, 1985 (FAI, 2007). Heavy metal contents of chemical fertilizers were compared with the required specifications by FAO/WHO (2001).

RESULTS AND DISCUSSION

The properties of the organic fertilizers, *viz.* moisture content, pH, EC, total organic carbon and C:N ratio, along with their range and mean values are presented in Table 1.

Moisture content

Considerable variation in moisture content was observed for the samples and the values ranged from 2.4 to 34.3 per cent, with a median value of 9.1 per cent. As per the quality control guidelines of city compost, the desired range of moisture content for organic manure is 15 to 25 per cent (Manna, 2004). While excessively dry products are dusty and unpleasant to handle, fertilizers with too much moisture become clumpy and increase transportation costs (Saha *et al.*, 2010). In this study, 13 per cent of the samples analysed showed moisture content higher than 25 per cent, and for majority of the samples it was less than 15 per cent.

pH and Electrical Conductivity

pH of the tested organic fertilizers ranged from 4.8 to 8.4, with a median value of 7.1. The desired range of pH for organic manures is 6.5 to 7.5, and 22 per cent of the samples tested complied with this range. Since majority of Kerala soils are acidic in reaction, organic manures with higher pH will have an advantage in increasing soil pH. Electrical conductivity varied from 4.0 to 7.8 dSm^{-1} with a median value of 5.6 dSm^{-1}. The threshold value of EC for a good quality compost is 4 dSm^{-1} (Manna, 2004). About 96 per cent of the samples tested had EC higher than this threshold value, indicating salt contamination.

Table 1. **Moisture, pH, EC, TOC and C/N ratio of organic fertilizers**

Sample no.	Moisture (%)	pH	EC(dsm^{-1})	TOC (%)	C/N Ratio
1	25.9	8.0	5.6	32.2	9.6
2	8.2	7.8	6.2	19.4	8.9
3	8.2	5.1	4.0	39.6	4.8
4	9.6	5.4	5.4	46.6	4.4
5	8.2	5.9	7.2	30.8	4.6
6	9.1	7.2	6.2	26.6	9.8
7	9.3	7.6	5.2	12.7	8.6
8	5.6	7.5	6.4	23.6	10.6
9	10.3	6.1	6.0	20.5	4.0
10	12.0	4.8	7.8	26.9	7.1
11	10.5	7.1	4.2	26.9	6.0
12	34.3	7.4	6.0	14.4	12.2
13	7.6	6.3	6.8	22.9	5.3
14	10.1	7.9	5.6	16.5	8.2
15	29.3	7.8	5.4	28.6	12.8
16	7.4	5.4	5.4	32.1	7.4
17	9.6	7.7	6.8	34.7	10.9
18	6.4	6.8	4.6	21.4	10.3
19	6.1	5.8	5.6	32.1	7.9
20	2.4	8.4	5.2	7.4	41.1
21	14.7	5.8	5.2	51.1	24.7
22	8.2	8.1	7.4	24.4	3.8
23	6.4	6.9	5.3	34.2	33.8
Range	2.4 - 34.3	4.8 - 8.4	4.0 -7.8	7.4 -51.1	3.9 - 41.1
Median	9.1	7.1	5.6	26.9	8.6
CV (%)	86.5	15.3	17.2	38.6	109.1
QC value for city compost as per FCO guideline	15 - 25	6.5 – 7.5	≤ 4	≥ 16	≤ 20:1

Organic matter content

Organic matter content in the fertilizer samples, expressed as total organic carbon (TOC) varied from 7.4 to 51.1 per cent, with a median value of 26.9 per cent. Organic matter content varied with respect to the source material used and this might be the reason for the wide variation in TOC.

C : N ratio

Optimum C to N ratio of good quality organic fertilizers is less than 20:1 (Manna, 2004). Wider C:N ratio results in immobilization of soil N and lower value results in loss of ammonia. Plants grown in fields applied with high C to N ratio composts are often yellow or stunted because of N deficiency arising out

Table 2 . **Nutrient contents of organic fertilizers**

Sample no.	N(%)	Total P(%)	Total K(%)	Total Ca(%)	Total Mg(%)
1	3.4	0.3	5.8	5.0	1.1
2	2.2	0.1	6.5	5.7	1.0
3	8.2	0.1	0.1	0.5	0.6
4	10.1	0.2	0.02	0.2	0.1
5	6.7	0.3	0.2	4.6	0.2
6	2.7	0.4	1.3	7.9	1.0
7	1.5	0.1	2.1	17.6	0.7
8	2.2	0.2	1.1	4.1	0.2
9	5.6	0.2	3.8	5.4	0.2
10	3.8	2.3	0.5	3.5	0.2
11	4.5	0.9	1.6	3.9	0.1
12	1.1	3.4	0.6	4.1	0.7
13	4.3	0.2	1.3	5.7	0.1
14	2.0	1.6	2.3	6.2	0.6
15	2.2	1.2	3.5	4.3	0.7
16	1.8	0.1	0.3	2.3	0.1
17	2.4	0.5	0.8	2.2	0.3
18	2.1	0.3	0.5	1.9	0.6
19	4.1	0.1	1.0	0.9	0.2
20	0.2	0.1	0.6	0.1	0.1
21	2.1	0.3	1.4	0.5	0.2
22	6.3	2.1	0.02	14.6	0.3
23	1.01	0.2	0.5	4.5	0.2
Range	0.2-10.1	0.1-3.4	0.02-6.5	0.1-17.6	0.1-1.1
Median	2.7	0.3	1.0	4.6	0.4
CV(%)	89.6	213.6	190.6	102.1	143.1
QC value for city compost as per FCO guideline	≥0.5	≥ 0.2	≥ 0.8	NA	NA

NA-Not available

of N immobilization in soil (Saha *et al.*, 2010). In the present study, C to N ratio of the fertilizer/manure samples varied from 3.9 to 41.1, with a median value of 8.6. Majority of the products had the desirable C to N ratio of 20:1. C: N ratio of composts is often more related to feed stocks, which is unknown for most of the products in the present study.

Major nutrients

The nutrient contents in the organic fertilizers, *viz.* total N, P, K, Ca and Mg are

Table 3. **Heavy metal contents in organic fertilizers (mg kg^{-1})**

Sample no.	Pb	Cd	Cr	Cu	Zn	Fe	Mn
1	7.7	0.38	8.6	47.7	137.2	4869.0	237.4
2	12.7	0.26	28.7	47.6	104.8	7920.3	187.7
3	8.4	0.08	3294.7	71.4	32.2	7274.8	47.7
4	9.5	0.02	2656.7	37.7	24.5	3704.5	27.6
5	8.2	0.42	1647.9	25.8	84.8	7152.3	69.2
6	10.9	0.53	160.7	39.9	327.3	5209.6	563.3
7	45.2	1.1	16.8	45.3	194.3	5087.8	393.4
8	104.3	0.63	82.3	263.1	415.0	21041.3	192.5
9	8.7	0.42	1563.7	11.8	69.6	6706.3	66.5
10	7.7	0.44	2595.9	16.8	32.7	7463.9	100.7
11	7.2	0.15	1816.6	14.2	40.4	5230.4	63.3
12	28.9	0.45	29.8	63.8	136.1	22961.2	599.8
13	10.7	0.29	2217.3	15.5	70.1	4872.7	55.4
14	10.3	0.50	2149.2	67.5	338.8	9612.6	264.8
15	11.9	0.35	25.6	32.4	154.4	5700.0	262.5
16	7.4	0.25	776.8	12.7	20.8	7216.4	69.0
17	7.5	0.04	31.9	35.5	98.3	11815.4	267.4
18	25.6	0.15	2202.9	30.7	65.1	8333.6	50.5
19	5.3	0.31	20.2	56.7	37.6	14886.2	66.7
20	4.7	0.42	9.8	22.4	65.4	2028.2	57.5
21	14.2	0.87	87.2	7.2	22.8	3814.0	59.6
22	9.4	0.63	14.5	3.5	99.8	1905.4	40.5
23	1.6	0.01	44.7	6.3	16.1	620.5	23.8
Range	1.6 -104.3	0.01 -1.1	8.6 -3294.7	3.5 -263.1	16.1 -415.0	620.5 -22961.0	23.8 -599.8
Median	9.4	0.38	87.2	32.4	70.1	5700	69.0
CV(%)	227.8	70.0	1265.1	161.1	156.5	99.9	143.1
QC value for city compost as per FCO guideline	≤ 100	≤ 5.0	≤ 50	≤ 300	≤ 1000	NA	NA

shown in Table 2. Nitrogen content varied from 0.2 to 10.1 per cent, with a median value of 2.7 per cent. Total P and K in the samples varied in the range from 0.1 to 3.4 per cent and 0.02 to 6.5 per cent, with a median value of 0.3 and 1.0, respectively. In general, the N, P and K content of organic manures is in the ratio 1: 0.5: 1, but can vary with varying substrate. The reason for the higher N, P and K contents, especially N, observed in some products is not clear, and fortification with chemical fertilizers may be the reason. Chemical analysis confirms only the nutrient contents, not the source and hence the

authenticity and integrity of the products coming in the market as "organic" fertilizer is a matter of concern.

Heavy metal contamination

Presence of heavy metals in the organic fertilizers/manures (Table 3) ranged between 1.6 to 104.3 mg kg^{-1} for Pb, 0.01 to 1.1 mg kg^{-1} for Cd, 8.6 to 3294.7 mg kg^{-1} for Cr, 3.5 to 263.1 mg kg^{-1} for Cu, 16.1 to 415.0 mg kg^{-1} for Zn, 620 to 2296 mg kg^{-1} for Fe and 23.8 to 599.8 mg kg^{-1} for Mn, and the corresponding median values are 9.4 mg kg^{-1} Pb, 0.38 mg kg^{-1} Cd, 87.2 mg kg^{-1} Cr, 32.4 mg kg^{-1} Cu, 70.1 mg kg^{-1} Zn, 5700 mg kg^{-1} Fe and 69.0 mg kg^{-1} Mn, respectively.

Chromium content was beyond the desirable limit of 50 mg kg^{-1} in 57 per cent of the samples and very high (1000-3200 mg kg^{-1}) in about 50 per cent of the samples tested as per FAI (2007). Chromium is present in pigments used in paints, inks and textile dyes and also in leather tanning wastes. Chromium is an environmental pollutant in the prevalent forms, *viz.* Cr (III) and Cr (V1). While Cr (III) has high potential for environmental contamination, especially aquifers and surface water. Chromium (V1) is classified as a Group A human carcinogen by US Environmental Protection Agency (Dhal *et al.*, 2013). Application of heavy metal contaminated fertilizers to agricultural soils is hazardous to man and environment. Since Cr is also phytotoxic, the effect of continuous application of these manures on soil Cr status is to be studied. Very high iron contents were observed in all the samples tested (Table 3) and permissible limit for iron is not fixed in FCO guidelines (FAI, 2007).

Comparison with quality control guidelines for city compost

The Fertilizer Control Order, 1985 has defined quality control (QC) parameters for city compost in India, for the purpose of regulating production and marketing. The

Table 4. **Percentage of samples complying with quality control parameters as per FCO guidelines for city compost**

Physico-chemical parameters	QC value	Within limit (%)	Below the limit (%)	Above the limit (%)
Moisture (%)	15-25	0	87	13
pH	6.5-7.5	22	39	35
EC(ds m^{-1})	d≤4	4	-	96
Total organic carbon (%)	e≥16	87	13	-
Total N (%)	e≥0.5		4	96
Total P (%)	e≥0.2	-	26	74
Total K (%)	e≥0.8	-	44	56
C:N ratio	d≤20:1	87	-	13
		Heavy metals		
Zn (mg kg^{-1})	d≤1000	100	-	-
Cu (mg kg^{-1})	d≤300	100	-	-
Cd (mg kg^{-1})	d≤5	100	-	-
Cr (mg kg^{-1})	d≤50	43	-	57
Pb (mg kg^{-1})	d≤100	96	-	4

Table 5. **Heavy metal contents in inorganic fertilizers (mg kg^{-1})**

Type of fertilizer	Pb	Cd	Cr	Cu	Zn	Fe	Mn
Rajphos (8)	26.1	3.1	0.2	27.2	59.3	2906.7	2672.0
Amophos (3)	13.4	5.3	47.5	22.4	200.6	2051.8	14.7
Single super phosphate (2)	17.3	5.9	54.3	11.3	107.3	7063.6	148.0
Triple super phosphate (2)	80.1	4.4	30.1	12.3	443.9	15437.5	1398.7
10:10:10 NPK mixture (3)	14.1	5.9	65.5	8.0	180.6	1101.6	288.7
18:18:18 NPK mixture (2)	13.0	3.0	54.8	3.8	55.7	2453.2	28.6
Diammonium phosphate (2)	9.1	16.4	238.5	40.5	440.0	5085.2	18.3
Urea (3)	1.6	ND	ND	1.3	1.3	22.4	0.6
MOP (3)	11.2	1.3	ND	1.6	ND	803.6	3.2
Magnesium sulphate (3)	13.1	1.3	ND	1.0	ND	5.0	6.1
Egyptian rock phosphate (25 % P_2O_5) (2)	14.1	15.7	38.2	6.3	203.2	1740.9	661.3
Egyptian rock phosphate (22 % P_2O_5) (2)	16.0	15.3	48.1	8.9	223.4	18367.4	671.9
FAO/WHO specifications	500	20	NA	NA	1850	NA	NA

ND – Not detected NA-Not available Figures in parenthesis are the number of samples

quality parameters determined in this study were compared with the QC values for city compost (Table 4) and observed that the extent of compliance varied widely with respect to different parameters. While majority of the samples conformed to the QC values with respect to total organic carbon, total N and C: N ratio, the extent of compliance for moisture content, pH and EC were poor. In the case of nutrients, QC values define only the minimum required N, P and K content, and there is no maximum allowable limit. Majority of the samples tested had N, P and K contents, especially N content, much above the minimum requirement as per QC value.

As for heavy metals, contents of Cd, Cu and Zn were within the QC limits in all the samples tested. Lead content was beyond the limit in only one sample. Chromium content was above the QC limit of 50 ppm in 57 per cent of the samples tested and extremely high (1000- 3200 mg kg^{-1}) in 50 per cent of the samples. Out of the 23 samples tested, the contents of Pb, Cd, Cr, Cu and Zn were within the limit in 13 samples only.

Heavy metals in inorganic fertilizers

Heavy metal content of fertilizers *viz.* rajphos, ammonium phosphate, single super phosphate, triple super phosphate, imported rock phosphates (Egyptian rock phosphates) and other fertilizers commonly used in Kerala *viz.* urea, muriate of potash, magnesium sulphate, and the fertilizer mixtures *viz.*10:10:10 and 18:18:18 are presented in Table 5. Permissible limits of heavy metals in inorganic fertilizers are not specified in Fertilizer Control Order, 1985, indicating that existing regulations are not strict enough regarding heavy metal contents (FAI, 2007). Therefore the data obtained was compared with the specifications of FAO/WHO (2001).

Mean Cd content in samples of rajphos was 3.1 mgkg,$^{-1}$ while that in imported rock phosphate was 15.4 mg kg^{-1}. However both these are within the limits specified by FAO/WHO (2001). Global pattern of Cd content in phosphate rocks ranged from 0.1 to 60 mgkg^{-1} (Javied *et al.*, 2009; Kpomblekou, 1994). Chromium content was also low in rajphos (mean value 0.2 mg kg^{-1}), while the

global range of Cr in phosphate rocks is 1 – 233 mg kg^{-1}. The study indicates the environmental advantage of indigenous rock phosphate. In FAO/WHO (2001) specifications, acceptable levels of Pb, Cd and Zn in inorganic fertilizers were 500 mg kg^{-1}, 20 mg kg^{-1} and 1850 mg kg^{-1}, respectively and all the tested samples were found to be well within the limits. Specifications for Cr, Cu, Fe and Mn are not available. However, high Fe contents were observed in all the P fertilizers.

CONCLUSION

The properties of the tested organic fertilizers varied widely with respect to different parameters, which could be due to the wide variety of source materials used for manufacturing the organic fertilizer. Majority of the samples contained nutrients, especially nitrogen, much higher than the minimum required quantity as per the quality control guidelines. About 50 per cent of the tested fertilizers contained high levels of chromium, and very high levels of iron. Continuous application of such metal contaminated materials to agricultural soils can lead to human health and environmental concerns in future. Presence of sand or powdered rock in the samples indicates mixing (adulteration) with such materials. The study shows the need for establishing quality control parameters for organic fertilizers of various origins, and regulating the quality of various products marketed as 'organic fertilizer'. Proper labeling of the contents with the explicit mentioning of "Permissible limits of Heavy Metals" should be made mandatory for all organic fertilizers/manures sold in the market.

Compared to the imported rock phosphates, rajphos showed low cadmium and high lead content. However, all these were within the limits specified by FAO/WHO (2001). Lead, cadmium and zinc contents in other inorganic fertilizers were also within the limits specified by FAO/WHO (2001).

ACKNOWLEDGEMENT

The authors would like to thank Sri. Antony. P. Antony, Assistant Scientific Officer and Sri. Shaheen. M, Scientific Assistant of Agronomy/Soils division for the assistance in instrumental and laboratory analysis.

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