REVISTA SCIENTIA AGRARIA
Versão On-line ISSN 1983-2443
Versão Impressa ISSN 1519-1125
SA vol. 17 n°. 2 Curitiba abril/maio. 2016 p. 1-13

AGRONOMIC AND INORGANIC PARAMETERS OF SEWAGE SLUDGE SANITIZED BY ALKALINE STABILIZATION: A CASE STUDY OF THE STATE OF PARANÁ, BRAZIL.

Parâmetros agronômicos e inorgânicos de lodo de esgoto higienizado por estabilização alcalina: um estudo de caso do estado do Paraná, Brasil

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Artigo enviado em 16/08/2016, aceito em 31/10/2016 e publicado em 20/12/2016.

Abstract – The agricultural use is an environmentally sustainable destination for sewage sludge because it promotes the recycling of nutrients and is beneficial to the cultivation of plants and to the physicochemical and biological characteristics of the soil. The Paraná is one of the Brazilian states where the sewage sludge has agriculture as a priority disposal. The composition of sewage sludge to be disposed for agricultural use is related to the sewer from which it was originated and the process of treatment of the sewage and of the sludge. The way of treatment and of hygienization affects the final characteristics of the sewage sludge. This case study aimed to evaluate the differences in composition of sewage sludge batches generated, in the Paraná, in systems containing anaerobic treatment and sanitized by prolonged alkaline stabilization, in relation to the agronomic and inorganic parameters (metals), from 2011 to 2013. Differences in the process of dewatering, hygienization and generation of batches, possibly, explain the differences of the agronomics parameters results verified between the batches produced in Sludge Management Units of the interior of the State, compared to the batches of the Curitiba Metropolitan Region. There was a large variability in the concentration of inorganic parameters of batches, probably associated to differences in sewage basins. Batches showed levels of inorganic parameters on average 89% below the limits of the State of Paraná, the Resolution of the State Environment Cabinet (Sema 021/09).

Keywords – biosolid, agricultural reuse, recycling, sanitation waste.

Resumo – O uso agrícola é uma destinação ambientalmente sustentável para o lodo de esgoto, pois promove a reciclagem de nutrientes, sendo benéfico ao cultivo de plantas e às características físico-químicas e biológicas do solo. O Paraná é um dos estados brasileiros onde o lodo de esgoto tem a agricultura como destinação final prioritária. A composição do lodo de esgoto a ser destinado para uso agrícola está relacionada com o esgoto que lhe deu origem e o processo de tratamento do esgoto e do lodo. A forma de tratamento e higienização afeta as características finais do lodo de esgoto. O presente estudo de caso teve por objetivo, avaliar as diferenças de composição de lotes de lodos de esgoto, gerados no Paraná, em sistemas contento tratamento anaeróbio e higienizados por estabilização alcalina prolongada, em relação aos parâmetros agronômicos e às substâncias inorgânicas, no estado do Paraná, no período de 2011 a 2013. Diferenças no processo de desaguamento, higienização e formação dos lotes possivelmente explicam as diferenças dos resultados de parâmetros agronômicos verificadas entre os lotes produzidos nas Unidades de Gerenciamento de Lodo do interior do estado, comparados aos lotes das Região Metropolitana de Curitiba. Houve grande variabilidade na concentração de substâncias inorgânicas dos lotes, provavelmente relacionada a diferenças nas bacias de esgotamento sanitário. Os lotes apresentaram níveis de substâncias inorgânicas em média 89% abaixo dos limites da Resolução da Secretaria Estadual de Meio Ambiente do Paraná (Sema 021/09).

Palavras-Chave – biossólidos, reuso agrícola, reciclagem, resíduo de saneamento.

INTRODUCTION

In Brazil, to the sanitation companies confront the challenge of adopting adequate procedures of treatment and final disposal of sewage sludge. This challenge has been consequence of the growth of urban areas, the expansion of the sewage collection networks, the implementation of more efficient treatment systems and the increasing pressure from environmental agencies.

The sewage sludge presents, in its constitution, significant amounts of organic matter, being beneficial to the physicochemical and biological characteristics of the soil (VARGAS; SCHOLLES, 2000; CHUEIRI et al., 2007; TRANNIN, SIQUEIRA; MOREIRA, 2007; MODESTO et al., 2009; De MARIA et al., 2010). It also has nutrients such as nitrogen (N) and phosphorus (P) favoring vegetal cultivation (WACHOWICZ; SERRAT, 2006; FRANCO et al., 2010; DE LUCIA et al; 2013; TEIXEIRA et al., 2015).

However, the residue may contain organic and inorganic pollutants, which must be controlled, when in agricultural use, so as not to negatively impact the environment (MARTINS, BATAGLIA; CAMARGO, 2003; BENABDALLAH EL-HADJ, DOSTA; MATA-ALVAREZ, 2006; TRABLY; PATUREAU, 2006; CAI et al., 2012; NOGUEIRA et al., 2013; SMIRI et al., 2015). Likewise, aiming the agricultural application, mitigation measures must be taken of pathogens, at levels that do not present risks to human health (MARTIN, BOSTAIN; STERN, 1990; SMITH, 1996; USEPA, 2003).

The criteria and procedures for agricultural use of sewage sludge in Brazil are set forth in the Resolution of the National Environment Council (Conama 375/06) (BRASIL, 2006). Among the procedures of the resolution are those related to licensing, sludge monitoring frequency, the elaboration of agronomic project, the conditions of handling, transport and application of the material. The document also sets out criteria for crops and agricultural areas able to receive the material, to locational restrictions, for defining application rate and for the monitoring of the application areas.

In Brazil, the application of sewage sludge in agriculture is restricted to a few states, such as São Paulo, Paraná, Rio Grande do Sul and the Federal District (SAMPAIO, 2013), and recently Espírito Santo.

In the state of Paraná, Brazil, the Sanitation Company of Paraná (Sanepar) destines the sludge generated in sewage treatment plants (STP) to agriculture, aiming to provide the final appropriate disposal under health, environmental and social aspects (BITTENCOURT et al., 2009). In the state, from 2011 to 2013, were generated about 57,492 t per year, in dry mass, of sludge and 107,416 t of hygienized sludge (total mass) were applied on 5,529 ha of agricultural land, the Curitiba Metropolitan Region (CMR) was responsible for 54% of this total (BITTENCOURT, 2014).

The agricultural reuse of sewage sludge follows the criteria and procedures established in Conama 375/06 and also of Resolution of the State Environment Cabinet - Secretaria Estadual de Meio Ambiente do Paraná (Sema 021/09) (PARANÁ, 2009). This Resolution defines Sludge Management Units (SMU) as a unit, linked or not to a STP, which performs the sludge management generated by one or more STP, for agricultural recycling. This resolution also set a maximum limit for pathogenic agents and inorganic contaminants. The monitoring of organic substances in the sludge is also required, but these do not have to adhere to maximum concentration limits. If any batch of sludge presents unsuitable characteristics for agricultural use in relation to sanity, the same goes for new hygienization and in case of not meeting the limits of inorganic substances, the alternative of disposal is landfilling for waste Class II - not inert.

The sewage sludge composition is related to the sewer from which it was originated and the process of treatment of the sewage and of the sludge. The way of treatment and of hygienization affects the final characteristics of the sewage sludge. Sludge, whose

REVISTA SCIENTIA AGRARIA
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SA vol. 17 n°. 2 Curitiba abril/maio. 2016 p. 1-13

stabilization and hygienization is done with alkaline material, have high pH and lower amount of nitrogen, due to volatilization losses of ammonia. Sludge in liquid form has more K, because it does not suffer dewatering in its production (BERTON; NOGUEIRA, 2010).

Given the scarcity of data on the characteristics of the sludge destined for agricultural use in Brazil, this case study aimed to evaluate the differences in the composition of sludge sewage batches in relation to the agronomic and inorganic parameters. The object of study was the sewage sludge produced in SMU of the CMR and in SMU of the interior of the State of Paraná, applied to agricultural land, from 2011 to 2013.

The study aims to present results that can be used as a subsidy in studies comparing with sludge generated in different locations or regions of Brazil, as well as those who have undergone by different treatment and hygienization processes, such as alkaline stabilization, composting and thermal drying.

MATERIALS AND METHODS

Study area

The state of Paraná has 399 municipalities, of which 191 possessed sanitary sewage systems in 2012, corresponding to about 310 million $m^3.year^{-1}$ of the treated sewage. Of this total, according to the National Sanitation Information System, Sanepar was responsible for the treatment of about 295 million $m^3.year^{-1}$, in 166 municipalities (BRASIL, 2012). Thus, because of the adopted disposal alternative, this case study is engaged in the agricultural destination of sludge generated in sewage treatment plants operated by Sanepar, from 2011 to 2013.

In 2012, the collected sewage was treated in 227 STP (SANEPAR, 2012), in which the biological treatment was in anaerobic reactors, like Upflow Anaerobic Sludge Blanket (UASB). Except for Belém STP, in Curitiba, with aerobic biological treatment in activated sludge system with extended aeration and the Audi industrial STP in São Jose dos Pinhais (which were not the subject of this study).

In all Paraná, in the STP with treatment containing anaerobic systems, UASB type, it was verified the existence of post-treatment units such as dissolved air flotation, trickling filter, polishing pond, aerated lagoon, anaerobic filter and submerged aerated filter. None of the STP, object of the present study, it was found the existence of primary sedimentation tank in operation.

In the most populous region of the state, the CMR, with 29 municipalities in 2012, the Sanepar operated 24 STP in 20 municipalities, in which 122,485 million $m^3.yr^{-1}$ domestic sewage were treated (BRASIL, 2012).

In 2013, the state of Parana had 81 SMU, composed of one or more STP, licensed by the state environmental agency, to carry out the management of the process of agricultural use of sewage sludge.

The object of this study was the sludge generated in STP with sewage treatment on systems containing anaerobic reactors, UASB type, with or without post-treatment units. The batches of sludge were dewatering in centrifuges in large STP and in drying beds in smaller STP and sanitized by prolonged alkaline stabilization (PAS).

The batch of sewage sludge is the amount of sewage sludge destined for agricultural use, generated by a SMU in the period between two subsequent samplings, physico-chemical and microbiologically characterized (PARANÁ, 2009).

In Parana State, the hygienization process of sewage sludge is used for prolonged alkaline stabilization (PAS), in which is added lime (CaO or CaO + MgO) in a proportion of 30 to 50% of total solids (TS) of the sludge. The pH is increased above 12, with a subsequent curing period of 30 days.

REVISTA SCIENTIA AGRARIA
Versão On-line ISSN 1983-2443
Versão Impressa ISSN 1519-1125
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After the hygienization, according to establishing the resolution, the batches were characterized regarding the agronomic parameters, sanity parameters, inorganic and organic substances. The collection of samples for laboratory analysis was carried out following the criteria established by Instruction n. 10/2004 of the Ministry of Agriculture, Livestock and Supply (Ministério da Agricultura, Pecuária e Abastecimento – MAPA) (BRASIL, 2004).

In this study, it was analyzed data from 100 batches of sewage sludge destined for agricultural use (47 of CMR and 53 of interior of the State), from 27 SMU covering 37 municipalities in the state.

The levels of bacteriological indicators and pathogens of de batches of Paraná destined for agricultural use in the period 2011 to 2013 corresponded to Class A sludge (PARANÁ, 2009). The Table 1 summarizes the results of the sanity parameters of batches used in this study.

Table 1 – Parameters of sanity of lots of sewage sludge produced in Paraná, applied in agricultural areas, from 2011 to 2013.

Parameters	Sema 021/09 Limit	Mean	Number of laboratory reports		
			Total	Results below QL	Results equal to zero
Thermotolerant coliforms (MPN.g_{TS}^{-1})	$<10^3$	364	100	79	2
Viable helminth eggs (.g_{TS}^{-1}))	<0,25	0,12	100	45	47
Salmonella sp. (in 10g-10 g_{TS}^{-1})	absence	-	100	26	74
Virus (PFU or FFU.g_{TS}^{-1})	<0,25	-	70	61	9

NOTE: Mean excluding the results equal to zero. QL- quantification limit of the laboratory analysis. MPN -most probable number. PFU- plaque forming units. FFU focus forming units.

Of the total 100 batches, 30 were not characterized as the virus (Table 1), a fact justified the state environmental agency considering the contracting laboratory analysis services with the required infrastructure and technical capacity (BITTENCOURT, 2014).

The Conama 375/06 and Sema 021/09 Resolutions establish a list of 34 organic pollutants to be determined, including quantitatively, in sewage sludge for agricultural use (Table 2). However, although there is no maximum concentration limits, when such organic substance are detected in the characterization of the batch, should be monitored the same substance in the soil at the criterion of the competent environmental agency. The Resolutions require that must be observed concentrations in soil contained in Table 2, which are similar to the guiding values for soil prevention established by the Environmental Company of São Paulo (CETESB, 2005).

Table 2 – Permissible concentration of organic substance in the soil under the Conama 375/06 and Sema 021/09 Resolutions and values prevention of Cetesb.

Substance	In the soil (mg kg^{-1})	
	Permissible concentration Conama 375/06 and Sema 021/09.	Value prevention Cetesb 2014
Chlorinated benzenes		
1,2-dichlorobenzene	0,73	0,7
1,3-dichlorobenzene	0,39	0,4
1,4-dichlorobenzene	0,39	0,1
1,2,3-trichlorobenzenes	0,01	0,01
1,2,4-trichlorobenzenes	0,011	0,01
1,3,5-trichlorobenzenes	0,5	0,5
1,2,3,4-tetrachlorobenzene	0,16	0,003
1,2,4,5-tetrachlorobenzene	0,01	0,01
1,2,3,5-tetrachlorobenzene	0,0065	0,006
Phthalate esters		
Di-n-butyl phthalate	0,7	0,1
Di(2-ethylhexyl) phthalate (DEHP)	1,0	1,0
Dimethyl phthalate	0,25	0,25
Phenols not chlorinated		
Cresols	0,16	0,2
Phenols chlorinated		
2,4-dichlorophenol	0,031	0,03
2,4,6-trichlorophenol	2,4	0,1
Pentachlorophenol	0,16	0,01
Polycyclic aromatic hydrocarbon (PAHs)		
Benz[a]anthracene	0,025	0,2
Benzo[a]pyrene	0,052	0,1
Benzo[k]fluoranthene	0,38	0,8
Indeno[1,2,3-c,d]pyrene	0,031	0,4
Naphthalene	0,12	0,7
Phenanthrene	3,3	3,6
Lindane	0,001	0,001
Persistent organic pollutants (POPs)		

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Versão Impressa ISSN 1519-1125
SA vol. 17 n°. 2 Curitiba abril/maio. 2016 p. 1-13

Aldrin	-	0,02
Dieldrin	-	0,01
Endrin	-	0,001
Chlordane	-	-
Heptachlor	-	-
Trichloroethane (DDT)	-	0,01
Toxaphene	-	-
Mirex	-	-
Hexachlorobenzene	-	-
PCBs	-	0,0003
Dioxins and furans	-	-

Because of the decrease in the frequency of the number of analysis of organic substances authorized by the state environmental agency, only six of batches of SMU of CMR were characterized as the organic substances. Of the 54 batches characterized, two had organic substances above the laboratory quantitation limit. The batch B produced in the CMR and the sludge batch of 2012 of the SMU Foz do Iguaçu (Table 3).

Table 3 – Organic substances detected in sewage sludge batches produced in Paraná, applied in agricultural areas from 2011 to 2013.

Substance	Concentration (mg kg^{-1})			
	Batch		Applied in the soil (theoretical)	
	B	Foz do Iguaçu	B	Foz do Iguaçu
Cresols	0,44	0,011	$1,3x10^{-3}$	$5,36x10^{-5}$
1,2-dichlorobenzene	0,03	-	$8,8x10^{-5}$	-
1,2,3-trichlorobenzenes	-	0,004	-	$1,95x10^{-5}$
1,2,4-trichlorobenzenes	-	0,004	-	$1,95x10^{-5}$
1,3,5-trichlorobenzenes	-	0,45	-	$2,19x10^{-3}$
Di-n-butyl phthalate	-	0,62	-	$3,02x10^{-3}$
Di(2-ethylhexyl) phthalate (DEHP))	-	0,51	-	$2,49x10^{-3}$
Dimethyl phthalate	-	0,41	-	$2,00x10^{-3}$
Dioxins and furans	$5x10^{-6}$	-	$1,5x10^{-8}$	-

The results of the theoretical calculation of the concentration of organic substances detected applied to the soil (Table 3) were well below the limit permitted by Conama 375/06 and Sema 021/09 Resolutions (Table 2).

Data analysis

The agronomic and inorganic parameters analyzed, were those established by Conama 375/06 (BRASIL, 2006), as shown in Table 4.

Table 4 – Agronomic and inorganic parameters and analytical methods used in the case study.

Agronomic parameters[1]	Inorganic parameters[2]
pH in water (pH_{H2O}), total organic carbon (TOC); total Kjeldahl nitrogen (TKN); ammonium (NH_4); Nitrate + Nitrite (NO_2+NO_3); total phosphorus (P); total potassium (K); total sodium (Na); total sulfur (S); total calcium (Ca); total magnesium (Mg); total solids (TS) and total volatile solids (TVS)	Arsenic (As); Barium (Ba); Cadmium (Cd); Lead (Pb); Copper (Cu); Chromium (Cr); Mercury (Hg); Molybdenum (Mo); Nickel (Ni); Selenium (Se); Zinc (Zn).

NOTE: [1]APHA et al. (2005), [2]Methods 3050 (USEPA 1996) and 3051 (USEPA 2007), established in SW-846.

The results of concentration of agronomic and inorganic parameters were obtained from laboratory reports of the companies contracted by Sanepar, to perform the characterization of the batch of sewage sludge for agricultural use. In this way, the results come from reports from eight different laboratories of the Paraná and São Paulo states.

In this case study, the treated sludge in SMU was grouped, forming two groups, as follows:

- CMR sludge batches, from three SMU of CMR;

- Interior of the State sludge batches, from 25 SMU in 23 municipalities of the Paraná.

Statistical analyzes were performed with the aid of Assistat software version 7.7 beta (SILVA, 2014). It applied to descriptive statistics. The Shapiro-Wilk normality test was used. For parameters with normal

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Versão Impressa ISSN 1519-1125
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distribution, it was applied the t-test, at 95% confidence, for mean comparison of the two treatments, using the completely randomized design with different numbers of replicates. For parameters that do not present normal distribution, it was applied the Mann-Whitney test to check if the treatments were different, at 95% confidence.

In the analysis of inorganic parameters were determined the 75th, 90th, 95th and 100th percentiles. In this determination, the limit of quantitation values were used for the results below these limits. In the calculation of coefficient of variation (CV) was not possible to obtain results for the parameters that were detected in less than four batches (SILVA, 2014). In the Mann-Whitney test were excluded for each parameter inorganic batches with values below the limit of quantitation values. It is noteworthy that the limit of quantitation values for the same parameter differed from laboratory to laboratory (Table 5). In the statistical analysis of the data parameter, zero replaced the results below 10^{-5}%.

Table 5 - Limits of laboratory quantitation checked in reports of different analytical laboratories for inorganic parameters that will present results below limit.

Parameter	Limits of laboratory quantitation (mg kg^{-1})	Number of reports with results below limit
As	0,001 - 0,01 – 0,04 - 0,7 - 0,8- 1- 3- 5- 10- 20	85
Ba	5 - 10	8
Cd	0,066 – 0,067– 0,071 - 0,072 - 0,082 - 0,086 – 0,092 - 0,095 - 0,098 – 0,099 - 0,1 - 1 - 2 - 5 - 10	46
Cr	1 - 5	2
Hg	0,0002 - 0,001 – 0,009 - 0,01 – 0,04 -0,05 - 10	68
Mo	0,1 - 0,4 - 0,7- 0,8- 1 - 5 – 6 - 10	57
Ni	1 - 10	2
Pb	4	2
Se	0,001 -0,01 - 0,1 – 0,4 - 0,5 - 0,6 - 0,7 - 0,8 - 0,9 - 1 - 2 - 5 - 10	92

NOTE: Arsenic (As); Barium (Ba); Cadmium (Cd); Lead (Pb); Copper (Cu); Chromium (Cr); Mercury (Hg); Molybdenum (Mo); Nickel (Ni); Selenium (Se); Zinc (Zn).

RESULTS AND DISCUSSION
Agronomics parameters

Table 6 presents the TS means of sludge batches destined for agricultural use in Paraná, from 2011 to 2013. The results for this parameter presented a normal distribution by Shapiro-Wilk test, and thus the t-test, at 95% confidence, was applied to compare means.

Table 6 - Means and coefficients of variation of total solids of sludge batches, generated in systems with anaerobic treatment and sanitized by prolonged alkaline stabilization, which were applied to agricultural land in Paraná, from 2011 to 2013

Parameter	CMR batches (n = 47)		Interior of Paraná batches (n = 53)		Total batches (n= 100)	
	Mean	CV	Mean	CV	Mean	CV
TS (%)	50.0 b	21.0	64.8 a	20.2	57.9	20.8

NOTE: Curitiba Metropolitan Region (CMR), n: number of batches analyzed, total solids (TS). The means followed by the same letter did not differ significantly. It was applied the t-test at 95% confidence.

Interior of the State sludge batches showed higher average of TS compared to CMR sludge batches (Table 6). Possibly are three factors that contributed to this result, which were mainly related to evaporation, among other factors. The first is related to the form of drainage. Of the 25 SMU of the interior of the State, 22 were dewatered in drying bed, while in the CMR, comparatively, greater amount of sludge was dewatered in a centrifuge, which results in a material with higher moisture content. The second factor is related to fewer batches per year in each Interior of the State SMU, causing the sludge permanence for a longer period, being stored until the close of the batch. The third factor is related to climatic conditions, since most of the Interior of the State SMU is located in temperate region, with hot summers, while the CMR is located in regions of mild summers (warmer monthly average of less than 22°C).

Bittencourt et al. (2014), in a study of CMR sludge batches, applied to agricultural land from 2007 to 2010, observed an average 51.7% of TS for batches generated in systems with anaerobic treatment, similar to the results of this study for sludge from CMR (Table 6). For the sludge generated in the treatment in activated sludge system with prolonged aeration, dewatered in presses and centrifugal and sanitized by PAS, the authors observed a significant lower content, of 34% of TS.

Table 7 presents the results of the other agronomic parameters of batches sludge, generated in systems containing anaerobic treatment and sanitized by prolonged alkaline stabilization, destined for agricultural use in Paraná, from 2011 to 2013.

Table 7 - Means and coefficients of variation of agronomic parameters of sludge batches, generated in systems with anaerobic treatment and sanitized by prolonged alkaline stabilization, which were applied to agricultural land in Paraná, from 2011 to 2013

Parameters	Unit	CMR batches (n = 47)		Interior of Paraná batches (n = 53)		Differents[1]	Total batches (n= 100	
		Mean	CV	Mean	CV		Mean	CV
pH_{H2O}	-	11.7	8.0	8.2	28.2	Yes	9.8	18.4
TVS	(% of TS)	18.3	51.0	31.0	37.0	Yes	25.0	42.4
TOC		12.0	67.9	16.4	66.7	Yes	14.3	68.5
TKN		0.9	83.5	2.3	60.7	Yes	1.7	70.1
NH_4		0.1	146.0	0.9	73.1	Yes	0.5	95.8
NO_2+NO_3		0.01	219.1	0.2	208.9	Yes	0.12	274.4
P		0.4	71.3	0.3	49.6	No	0.4	63.7
K		0.10	141.7	0.07	176.2	Yes	0.08	158.9
Ca		12.4	32.4	10.3	115.8	Yes	11.3	81.4
Mg		7.0	35.0	2.2	158.7	Yes	4.5	69.9
S		1.0	98.0	0.8	184.6	No	0.9	141.6
Na		0.09	115.2	0.12	289.7	No	0.1	248.4

NOTE: Curitiba Metropolitan Region (CMR), n: number of batches analyzed, pH in water (pHH2O), total organic carbon (TOC); total Kjeldahl nitrogen (TKN); ammonium (NH4); Nitrate + Nitrite (NO2+NO3); total phosphorus (P); total potassium (K); total sodium (Na); total sulfur (S); total calcium (Ca); total magnesium (Mg); total solids (TS) and total volatile solids (TVS) . [1]It was applied the Mann-Whitney test to check if the treatments were different, at 95% confidence. The calculation considered the detection limits for results below those limits.

Table 7 shows that the average pH, TVS, TOC, TKN, NH_4, NO_2+NO_3, K, Ca and Mg of the Interior of the State sludge batches were different from those of the CMR sludge batches. There were lower mean of pH, Ca and Mg in the Interior of the State sludge batches, probably due to differences in the hygienization and generation of batches process. The lime dosage applied in batches of the state of the Interior of the State was near 30% relative to TS of sludge, while for the CMR this dosage was about 50%.

Furthermore, in most of the Interior of the State SMU, it was formed only a batch per year, having many batches that have received the mixture of lime 10 to 11 months before the batch, was closing up, during this period, it probably happened the lowering of the pH. The pH decreased in sewage sludge, because it is a material rich in organic matter, which results from the formation of organic acids and nitrification reactions of the ammonium (YAN, SCHUBERT; MENGEL, 1996).

The pH average is not maintained at level 12 until the time of characterization of the batches (Table 7), fact which was not affect in the sanitation thereof, since the batches showed results of sanity parameters below the limits of the Sema 021/09 (PARANÁ, 2009).

The Interior of the State batches presented means of TVS, TOC, TKN, NH_4 and NO_2+NO_3 higher than those of the CMR sludge batches (Table 4).

The highest K content in Interior of the State batches may be related to lower TS content of these batches (Table 7), since the nutrient is soluble. The average of P, S and Na in Interior of the State batches were not different from those of the CMR sludge batches (Table 7).

The means obtained in this study (Table 7) for the sludge from CMR, were similar to those reported by Bittencourt et al. (2014) in a study of CMR sludge batches, destined for agricultural use, from 2007 to 2010, for the parameters pH, TVS, TOC, P, K and Ca, respectively, 11.5; 21.9%; 11.7%; 0.4%; 0.1% and 13.4%.

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Versão On-line ISSN 1983-2443
Versão Impressa ISSN 1519-1125
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Inorganics parameters (metals)

Table 8 shows the comparison between the limits of Sema 021/09 with percentiles 75, 90, 95 and 99 for evaluated inorganic parameters of the batches, which the calculation considered the limit for quantification results below those limits. The following results of inorganic parameters refer to batches of sludge destined for the agricultural use in 2011 to 2013 in Paraná.

Table 8 - Percentiles 75, 90, 95 and 99 of the inorganic parameters of batches of sludge generated in systems with anaerobic treatment and sanitized by prolonged alkaline stabilization, applied to agricultural land in Paraná, from 2011 to 2013, compared to the limits of Sema 021/09.

Inorganic parameters		Percentile 75	90	95	99	Sema 021/09
As	$mg.kg_{TS}^{-1}$	1.6	10	10	20	41
Ba		235	438	897	1175	1300
Cd		6.4	13	17	32	20
Cr		40	63	106	267	1000
Cu		158	251	426	763	1000
Hg		0.86	10	10	10	16
Mo		5.85	10	12	36	50
Ni		53	67	77	166	420
Pb		77	125	164	329	300
Se		1	10	10	23	100
Zn		537	695	887	1028	2500

NOTE: Arsenic (As); Barium (Ba); Cadmium (Cd); Lead (Pb); Copper (Cu); Chromium (Cr); Mercury (Hg); Molybdenum (Mo); Nickel (Ni); Selenium (Se); Zinc (Zn). Calculation considering the detection limits for results below those limits.

It can be seen (Table 8), that the 99th percentile of Cd exceeded the limit of Sema 021/09. This happened to two batches of sludge, with concentrations of Cd of 27.3 and 32 $mg.kg_{TS}^{-1}$ due to a misconception of analysis of the responsible managers, who compared the results of the laboratory reports with the limits of Conama 375/06, of 39 $mg.kg_{TS}^{-1}$ for Cd and liberated the batches for agricultural use. However, it is noteworthy that the accumulated load limit of both Resolutions, of 4 $kg.ha^{-1}$ (BRASIL, 2006; PARANÁ 2009), was not exceeded, being of 0.097; 0.30 and 0.35 $kg.ha^{-1}$ in the areas that received these batches of sludge.

In Paraná, the sanitation concessionaire, Sanepar, accepts only the disposal of industrial wastewater in the domestic sewer collection network, by conformity of effluent quality criteria by industries. Values are set limits for: BOD, COD, pH, temperature, oil and grease, settleable solids, N, P, Ag, As, Cd, Cr, Cu, soluble Fe, Hg, Ni, Pb, Se, Sn, Zn, benzene, cyanide, chloroform, dichloroethane, styrene, etibenzeno, phenol, fluoride, sulfate, sulfite, surfactants, carbon tetrachloride, toluene and xylene. Managers can establish more restrictive limits, based on local evaluation of capacity of sewerage systems and of STP (SANEPAR, 2013).

The average of the average of inorganic content of sludge batches, destined for the agricultural use, was 89% below the limits established by Sema 021/09 (PARANÁ, 2009) (Table 9). Fact that demonstrates the safety in the agricultural use of sludge produced in the state of Paraná and that demonstrates that the control of receiving industrial effluents in the domestic sewage network is effective to obtaining sludge with low levels of inorganic substances.

Table 9 - Average of percentages of means of concentrations of inorganic parameters below the limit of Sema Resolution 021/09, of batches of sludge generated in systems with anaerobic treatment and sanitized by prolonged alkaline stabilization, applied to agricultural land in Paraná, 2011-2013

Inorganic parameters	As	Ba	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn	Mean
% Below the limit of Sema 021/09 (%)	95	82	78	69	87	89	92	92	82	98	83	89

NOTE: Arsenic (As); Barium (Ba); Cadmium (Cd); Lead (Pb); Copper (Cu); Chromium (Cr); Mercury (Hg); Molybdenum (Mo); Nickel (Ni); Selenium (Se); Zinc (Zn). Calculation considering the detection limits for results below those limits.

Table 10 contains the minimum, maximum and average concentrations, coefficients of variation and the number of laboratory reports analyzed for each inorganic parameter, for this statistical analysis, the reports presenting laboratory results below the limit of quantification were excluded.

REVISTA SCIENTIA AGRARIA
Versão On-line ISSN 1983-2443
Versão Impressa ISSN 1519-1125
SA vol. 17 n°. 2 Curitiba abril/maio. 2016 p. 1-13

Table 10 Minimum, maximum and mean concentrations, coefficients of variation and number of reports, of batches of sludge generated in systems with anaerobic treatment and sanitized by prolonged alkaline stabilization, applied to agricultural land in Paraná, 2011-2013, with results above the analytical detection limit

Inorganic parameters	Minimum ($mg.kg_{ST}^{-1}$)	Maximum ($mg.kg_{ST}^{-1}$)	Mean ($mg.kg_{ST}^{-1}$)	CV (%)	Number of reports	Sema 021/09 ($mg.kg_{TS}^{-1}$)
As	0.1	10	2.4	95.9	15	41
Ba	25	1175	251	90	92	1300
Cd	0.5	32	7.8	84	54	20
Cr	3.6	267	38	116	98	1000
Cu	1.7	764	129	103	100	1000
Hg	0.03	2.76	0.8	70	31	16
Mo	0.41	36	5.6	115	43	50
Ni	3.7	167	35	80	98	420
Pb	4.7	330	55	101	98	300
Se	4.9	23	10	55	8	100
Zn	67.2	1028	424	50	100	2500

NOTE: Arsenic (As); Barium (Ba); Cadmium (Cd); Lead (Pb); Copper (Cu); Chromium (Cr); Mercury (Hg); Molybdenum (Mo); Nickel (Ni); Selenium (Se); Zinc (Zn).

Parameters As and Se were detected, respectively, in 15% and 8% of the batches (Table 10). Directive 86 /278/EEC of the European Union do not require the monitoring of these substances in biosolids (COUNCIL OF THE EUROPEAN COMMUNITIES, 1986).

There were high coefficients of variation in the results of concentration of inorganic parameters in the batches (Table 10). According Berton and Nogueira (2010), there is great variability in the concentration of inorganic substances in sewage sludge generated in different STPs, fact checked at the results of characterization of sewage sludge from Barueri STP, located in the Metropolitan Region of São Paulo, with high rates of industries. According Pegorini et al. (2006), in a survey of 40 sewage sludge samples from Paraná State, undue industrial discharges in the sewage collection networks may account for the large variation in the concentration of inorganic parameters.

Table 11 shows the average of inorganic parameters of batches of sludge that had concentrations above the laboratory quantitation limit, destined for agricultural use in Paraná, from 2011 to 2013. The total number of batches was 47 and 53, respectively, of CMR and of Interior of Paraná. The concentrations of inorganic parameters of these batches do not present normal distribution. In this way, the Mann-Whitney test was applied to determine the difference between treatments at 95% confidence, as shown in Table 11.

Table 11 - Means of inorganic parameters of sludge batches, generated in systems with anaerobic treatment and sanitized by prolonged alkaline stabilization, applied to agricultural land in Paraná, from 2011 to 2013, which showed results above the laboratory detection limit

Inorganic parameters	Mean ($mg.kg_{TS}^{-1}$)		Number of reports		CV (%)		Differents[1]
	CMR	Interior of Paraná	CMR	Interior of Paraná	CMR	Interior of Paraná	
As	2.2	3.4	12	3	47.4	-	No
Ba	160.5	319.9	40	52	38.0	86.5	Yes
Cd	1.3	8.9	8	46	42.5	72.1	Yes
Cr	27.0	48.2	45	53	58.0	118.8	Yes
Cu	69.3	183.2	47	53	35.1	89.6	Yes
Hg	0.83	0.03	30	1	66.2	-	Yes
Mo	3.8	7.4	21	22	66.0	112.8	No
Ni	16.9	51.1	45	53	53.3	57.9	Yes
Pb	20.2	86.9	47	51	56.8	69.5	Yes
Se	12.2	6.8	5	3	48.9	-	Yes
Zn	392.1	451.7	47	53	46.5	51.1	No

NOTE: Curitiba Metropolitan Region (CMR);Arsenic (As); Barium (Ba); Cadmium (Cd); Lead (Pb); Copper (Cu); Chromium (Cr); Mercury (Hg); Molybdenum (Mo); Nickel (Ni); Selenium (Se); Zinc (Zn).

[1]It was applied the Mann-Whitney test to check if the treatments were different, at 95% confidence. Calculation excluding the concentrations below the analytical detection limit.

The averages of Interior of Paraná batches, to the inorganic parameters: Ba, Cd, Cr, Cu, Ni and Pb were higher than the average of the batches produced in CMR (Table 11). Pegorini et al. (2006) observed higher values in sewage sludge in Parana, to the Cr, Cu, Ni, Pb and Zn in the regions derived from basalt rock, whose soil typically contains higher concentrations of these elements. For Hg and Se the average concentrations of CMR batches was higher than the Interior of Paraná batches.

CONCLUSIONS

The present study showed the results of the characterization of 100 batches of treated anaerobic sludge from different locations in Paraná. These results serve to support in comparative studies of sludge generated in locations or regions distinct, since that considered the difference between the methods of treatment and hygienization they were submitted. These values presented also may guide professionals responsible for developing of the agronomic projects for the agricultural use of sludge. In this case it was observed that:

- In Paraná, Brazil, the batches of sewage sludge produced, from 2011 to 2013, in Interior of State, compared to CMR batches, had lower means of pH, K, Ca and Mg, highest means for TS, TVS, TOC, TKN, NH_4, NO_2+NO_3 and there were no difference between the means of P, S and Na.

- Batches of sewage sludge showed concentrations of inorganic parameters, on average, 89% below the limits of Sema 021/09 Resolution. Fact that demonstrates that the control of receiving industrial effluents in the domestic sewage network is effective to obtaining sludge with low levels of inorganic substances.

- There was great variability in the concentrations of the inorganic parameters analyzed. The means of the batches of the Interior of State were higher for Ba, Cd, Cr, Cu, Ni and Pb and lower for Hg and Se compared to the means of CMR batches, in the period analyzed. For other inorganic parameters, there were no differences between their means.

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