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Research Article

Wastewater Treatment Plants as Producer of Alternative Fertilizers for Agriculture in Spain: a Case Study (WWTP of La Golondrina -Córdoba, Spain)

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Abstract

Europe's Mediterranean countries have a serious problem with respect to supply for effective and safe fertilizers as in the case of Spain. In this way, since 1990 Spanish count with regulations to allow the safe use of bio-solids produced in the WWTP in agriculture: they are a valuable by-product, which concentrate the pollution present in urban wastewater. Production of bio-solids in Spain achieves more than 700.000 T/year (matter dried) and around 80% of these ones are sent to be used in agriculture as alternative fertilizer. This practice can be carried out by the fact that bio-solids have an important content in organic matter, N, P and, in minor level, K. To preserve soils, all bio-solids used in agriculture must not contain more quantity of heavy metals than those established in the Spanish regulations for Cd, Cu, Ni, Pb, Zn, Hg and Cr. In the case of La Golondrina´s WWTP, our study has been extended for 2000-2019: in this period the facility has treated a mean flow of 26.55x106 m3/year and has produced 38,000 T/year of bio-solids with 74.9% of organic matter over dried mass. On the other hand, concentrations of the seven metals limited in the Spanish normative have been respected in time. Moreover, from viewpoint to potential use for agriculture, major components of bio-solids were N, P (as P_2O_5) and Ca (as CaO) which levels were 6.6%, 3.5% and 3.7%, respectively, as well as K (as K_2O) with 0.6%, over dried matter. Finally, our biosolids have always in accordance with the Spanish regulations and have been used for agriculture without problems.

Introduction

Agricultural soils in Europe's Mediterranean countries have a serious problem with respect to supply for effective and safe fertilizers, as in the case of Spain. Progressive process of desertification removes nutrients from soils enough quickly, such as organic matter, N, P and K, and other micronutrients, yielding towards an unfavorable scenario for environmental and agricultural sustainability. According the last estimates and statistics for this purpose [1] Spain (47,000,000 inhabitants) have around 1,700 WWTP, of which a 63% have in addition to primary treatment, a biological treatment (secondary treatment) and a 33% have a final chemical or disinfection treatment (tertiary treatment). Production of bio-solids in Spanish WWTP [1,2] is around 3,000,000 T/year of total matter, with a 25% of dried matter over total. Moreover, around 80% of total produced biosolids are used directly in agronomy or sent to composting with urban solid waste [1-3]. The rest of bio-solids are disposed in controlled dump (11%) and used in electric production (9%).

On the other hand, use of bio-solids in Spain is based in two regulations: the RD 1310/1990 (regulation translated from EU) [4] and the O.M. AAA 1072/2013 [5]. Here are established parametric values that must comply bio-solids for its potential use in agronomy. Almost, in the RD 1310/1990 are specified two distinct levels to respect heavy metals, by considering two type of soils: soils with pH<7 (acidic soils) and basic soils with pH>7. These levels are of obligatory compliance. Likewise, of all the rest of parameters considered in regulations do not have established limiting parametric values, they should be only investigated. In basis to the above, the aim of this paper will be to show the quality of bio-solids of a great WWTP of Spain during the last 20 years and evaluate the correspondence or not of its quality with respect to Spanish current regulations. Bio-solids can be an alternative fertilizer to those specific to Spanish agriculture.

Materials and Methods

Samples of bio-solids were extracted monthly, during the first five days of each month. pH and conductivity of bio-solids were measured by using the common methods used in soils analysis [6-8]. Metals were determined by Inductive Coupled Plasma-Mass Spectrometry system after digesting bio-solids with 3mL of HCl, 1 mL of HNO_3 and 20 mL of water. Nitrogen was determined according to Kjeldahl´s method and total phosphorous also by ICP-MS after digesting the sample with ammonium persulfate in sulphuric medium. Moreover, dried matter was obtained by drying the sample to constant weight to 105-108ºC, and the organic matter by heating to 550ºC also up to constant weight. Investigations of microbiology of bio-solids (filtration method and plate culture with chromogenic media) were carried out to filtrate obtained after suspending bio-solids with 100 mL of sterilized water maintained during 30 minutes of contact [9-11].

Results and Discussion

La Golondrina´s WWTP, within the 80 largest treatment plants in Spain, is a conventional facility which operating line is the following: elevation of raw wastewater to plant by Arquimedes´s screws, screening (two lines of 10 and 5 cm of opening size), primary settling without addition of chemical reactants, aeration and biological treatment (activated sludge), secondary settling and finally, disposal to river. The plant could actually treat up to 145,000 m^3/day of municipal wastewater [12-14]. Almost, since 2015 there has been applied ferric salts to pre-treat an industrial effluent with very little biodegradability received in plant (yeast

Table 1: Characteristics of biosolids: regulations applied in Spain and parametric values (1) average quality for Spanish biosolids and (2) average quality for biosolids of La Golondrina´s WWTP (2000-2019 period).

Parameter	Units	RD 1310/1990	OM AAA 1072/2013	-1	-2
Dryness	% o.i.mass[1]	Not included	Unlimited	-	22.3
Organic matter	% o.d.mass[2]	Not included	Unlimited	72	74.9
pH	pH units	Not included	Unlimited	6.74	6.4
Total-N	% of N	Not included	Unlimited	4.0 – 5.0	6.6
C/N	Organic matter/ total N	Not included	Unlimited	-	16.4
Ammonium-N	% of NH_4[3]	Not included	Unlimited	-	5
Total-P	% of P_2O_5[3]	Not included	Unlimited	0.6 – 5.0	3.5
K	% of K_2O[3]	Not included	Unlimited	0.2 – 1.0	0.6
Ca	% of CaO[3]	Not included	Unlimited	5.0 - 14.0	3.7
Mg	% of MgO[3]	Not included	Unlimited	0.8	0.6
Na	% of Na[3]	Not included	-	-	0.1
Fe	mg/kg o.d.m[4]	Not included	Unlimited	16,821	11,749.10
Mn	mg/kg o.d.m[4]	Not included	-	-	265.7
Cu	mg/kg o.d.m[4]	1,000[a] – 1,750[b]	-	248	392.8
Pb	mg/kg o.d.m.[4]	750[a] – 1,250[b]	-	77.8	64.3
Cd	mg/kg o.d.m.[4]	20[a] -40[b]	-	<0.1	16.8
Ni	mg/kg o.d.m[4]	300[a] – 400[b]	-	42.7	21.6
Cr	mg/kg o.d.m[4]	1,000[a] - 1,500[b]	-	135.3	44.3
Zn	mg/kg o.d.m[4]	2,500[a] – 4,000[b]	-	712	463.1
Hg	mg/kg o.d.m[4]	16[a] – 25[b]	-	1.2	1.4
Salmonella	Pres./Abs. per 25 g/biosolids	Not included	Unlimited	Presence	Presence
Escherichia coli	Colony-forming units, per g/ biosolids	Not included	Unlimited	$<10^2$ - $>10^8$	$4{,}1\times10^8$

(1) o.i.mass: over initial mass; (2) o.d.mass: over dried mass; (3) % of Ammonium, P, K, Ca and Mg over dried mass; (4) mg/kg o.d.m.: mg/kg over dried mass; (a) RD 1310/1990 soils pH<7; (b) R1310/1990 soils pH>7.

Table 2: Maximum values measured of metals and % over parametric value (acidic soils).

Metal	Maximum value	% over parametric value, soils pH<7
Cu mg/kg o.d.m.	738.5	74%
Pb mg/kg o.d.m.	262.5	35%
Cd mg/kg o.d.m.	15	75%
Ni mg/kg o.d.m.	62	21%
Cr mg/kg o.d.m.	202.5	20%
Zn mg/kg o.d.m.	820	33%
Hg mg/kg o.d.m.	3	19%

factory). Table 1 shows average characteristics of bio-solids obtained in our study (2000-2019), average characteristics of Spanish biosolids according bibliography and the two regulations applied in Spain to establish the use or not of bio-solids in agronomy.

In the case of heavy metals included in the RD 1310/1990 [4], the limiting parametric values have two levels according to pH of soils: in acidic soils and because the high mobility of metals in this media, levels are lower than those of basic soils. It can be noted that all the rest of parameters considered (OM AAA 1072/2013) [5] must be investigated in bio-solids but have not established limit. At the same time, if the heavy metals levels

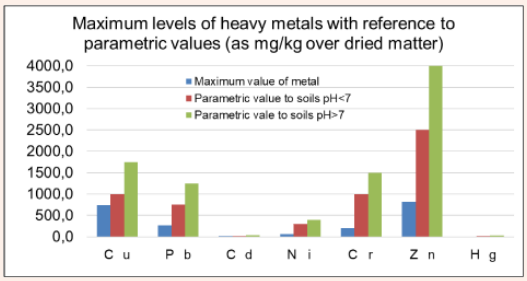

Figure 1: Maximum values of metals along 2000-2019 (blue); parametric values for acidic soils (red); parametric values for basic soils (green).

have been exceeded in bio-solids these should considered as dangerous waste and should not be used as fertilizers. Results showed in Table 1 for La Golondrina´s WWTP bio-solids indicate average values of dried matter of 22.3% and those of organic matter over dried matter equal to 74.9% this implies an important amount as fertilizer existing in bio-solids. On the other hand, average of % Total-N exhibited a mean value of 6.6%, while average of % Total-P (as P_2O_5) of bio-solids ranged 3.5%. Finally, middle value of K in bio-solids are moderate enough, ranging 0.6% as K_2O.

Considering now the situation of alkaline and alkaline-terrous metals present in bio-solids, Ca, K (above commented) and Mg should have positive agronomy significance, and on the contrary, Na can have negative influence because it could provoke salinization of soils. In any case, the majority metal was Ca with a mean value of 3.7%. With respect to K, its main value was 0.6% and finally, the result for Mg was very similar to that of K (mean value 0.6% as MgO), and in the case of Na, the mean value was only 0.1%: thus, the affection over salinization of soil was not amountable. On the other hand, total concentration of heavy metals investigated in bio-solids has exhibited a mean value of 13,006 mg/kg o.d.m., being the majority metal Fe (more than 11,000 mg/kg o.d.m. and which origin has been commented above). Minor amounts were found of Zn (463 mg/kg o.d.m.), Cu (393 mg/kg o.d.m.) and Mn (266 mg/kg o.d.m.) this last one not included in regulations. Ultimately, the minority metal measured was mercury with just over 1 mg/kg o.d.m.

We can now evaluate the compliance of the seven metals limited in the Spanish regulations to use in agronomy of bio-solids. It can be observed according of above Table 1 than mean values of Cu, Pb, Cd, Ni, Cr, Zn and Hg are far below of parametric value (for both, acidic and basic soils). Nevertheless, to check the compliance in the most unfavorable conditions, we can compare the maximal values of each metal with the most restrictive regulations (acidic soils). Thus, in Figure 1 is shown the maximal values obtained for all the seven limited metals along the period 2000-2019 against its parametric values: all values have been lower enough than its parametric values, to use in both, soils with pH lower than 7, and soils with pH higher than 7.

As complementary information, Table 2 shows maximum values for each metal and its % with relation to parametric value in acidic soil. It can be seen than in all the cases were respected the imposed limits. With respect to microbiology of bio-solids, regulations only indicate the investigation of Salmonella and Escherichia coli, without any parametric value. We can read in above Table 1 that Salmonella always has been present in bio-solids (25g of sample), as well as the average amount for Escherichia coli was 4.1×108 colony-forming unit per g, with a maximum of 1×109.

To finish this paper can be very interesting to compare the characteristics of bio-solids studied against the dates existing in bibliography about bio-solids obtained in several Spanish WWTP (Table 1) [1,2,3]. So, we can conclude that organic matter, pH and agronomic parameters (N, P, Ca, Mg and K) are very similar. With relation to heavy metals, all dates have the same order of magnitude. Moreover, Fe, Ni, Cr and Zn show levels lower in our case than in the rest of Spain; oppositely, Cu, Cd and Hg are higher in our study. This evidence is related with the different characteristics of urban wastewater in Spain. Finally, in all the bio-solids (Spanish and case study) was present Salmonella, while there was a large dispersion of results about Escherichia coli.

Conclusion

a) Pollution existing in urban wastewater is converted after its transit through a Waste Water Treatment Plant, in a reusable substrate named bio-solids, because to its important content in organic matters and nutrients.

b) Thus, our survey during 2000-2019, demonstrated that these bio-solids showed 74.9% of organic matter over dried mass and content of N, P (as P_2O_5) and Ca (as CaO) of 6.6%, 3.5% and 3.7%, respectively, as well as 0.6% of K (as K_2O) over dried matter.

c) On the other hand, concentration of the seven metals limited in the Spanish regulations to use of bio-solids in agriculture (Cu, Pb, Cd, Ni, Cr, Zn and Hg) has been respected in time in both, use for acidic soils, and for basic soils. Even more, maximum levels in the last twenty years have been lower than those of the maximum parametric values.

d) At the same time, microbiologic content of bio-solids exhibited presence of Salmonella and high levels of Escherichia coli, but this circumstance do not restrict its use for agriculture.

e) Finally, characteristics or La Golondrina´s WWTP are very similar to those of bio-solids produced in the great majority of Spanish WWTP.

f) As major conclusion, bio-solids produced in the Spanish WWTP can aid to minimize the existing problem about to have alternative effective and safe fertilizers for agriculture distinct of the conventional ones.

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