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Research Article

Quality of bio-solids produced in a Spanish Wastewater Treatment Plant (Córdoba-Spain) and its use in agronomy along 2000-2019

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Abstract

Bio-solids are the final fate of pollution present in urban wastewater, reaching the production of these ones in Spanish WWTPs 701,751 T/year (dates of 2018). Considering that 85% of Spanish bio-solids are used in agronomy, it is important to know characteristics of biosolids there produced, and in this way, we have investigated bio-solids generated in La Golondrina´s WWTP (Córdoba, Spain) along 2000-2019. This WWTP is a conventional facility operated by activated sludges (26.55x10^6 m^3/year treated) which has produced 1.43 kg of bio-solids per m^3 of treated wastewater (38.000 T/year). Our results indicated that bio-solids had a dryness over initial mass of 22.3%, and 74.9% of organic matter over dried matter (o.d.m.). At the same time, major components detected in bio-solids were N, P and Ca which levels were 5.0%, 3.5% and 3.7%, respectively. On the other hand, concentration of total metals in bio-solids ranged 13,024 mg/kg o.d.m., being the main metal Fe (11.749 mg/kg o.d.m.) followed by Zn, Cu and Mn, with levels as mg/kg o.d.m. of 463.1, 392.8 and 265.7, respectively. Evolution per year of all the investigated parameters are shown in the paper. Taking into account the use of bio-solids in agronomy, we have evaluated levels of metals limited by the Spanish normative to this respect: thus, the seven metals restricted (Cd, Cu, Ni, Pb, Zn, Hg and Cr) exhibited concentration in bio-solids very lower than parametric values established. Moreover, we have estimated the ratios of accumulation of organics and metals from wastewater to bio-solids: thus, organic matter, N and P, were accumulated in bio-solids respectively, 342, 356 and 643 times, and total metals, 2,632 times. Finally, levels of *Escherichia coli* slightly varied from wastewater to bio-solids: 1.5x10^8 colony-forming units/L in the first one, and 0.9x10^8/g (o.d.m.) in the second ones.

Keywords: urban wastewater, Wastewater Treatment Plant (WWTP), biosolids, organic matter, chemical wastewater treatment, louds metals, nitrogen, phosphorous, potassium.

1.Introduction

In previous paper [1] we showed results obtained in the characterization of bio-solids generated in the WWTP of La Golondrina (Córdoba-Spain) along 2002-2003. This WWTP treats municipal wastewater of Córdoba city (then, 325,000 inhabitants) located in the south of Spain. The facility receipts all the domestic and industrial wastewater of the town (15% of industrial wastewater) carrying out the treatment by means biological aerated process through active sludges [1,2,3]. Taking into account that the treatment of wastewater implies the transfer and concentration of original pollution existing in wastewater towards bio-solids, we paid also attention to this subject.

In a second study along 2001-2006 [2] we obtained that each m^3 of urban wastewater influent to La Golondrina´s WWTP was converted in 1.6 kg of bio-solids, with a dryness of 21.9% (over total mass) and a mean level of organic matter of 73.9% (over dried matter).

Above studies, also, concluded that the raw municipal wastewater contained 2.7 mg/L of total metals after heat digestion, being iron the major metal (1.5 mg/L) followed by copper, zinc, manganese, lead, chromium, nickel and cadmium. Each litter of raw wastewater contained 500 mg of organic matters (biodegraded matter, i.e., matter measuring as BOD_5). On the other hand, treated wastewater showed 1.4 mg/L of total metals being also iron the major metallic specie detected, followed now by lead and chromium, copper, nickel, cadmium, manganese, zinc and mercury.

Production of bio-solids in La Golondrina´s WWTP [1,2,3] follows a conventional process: thus, sludges removed in both primary and secondary treatment (<0.05% of dried matter) are concentred by floating (secondary sludges) or gravity (primary sludges) decanters up to lead 3-5% of dried matter. These dried sludges are latter dehydrated in two phases: firstly, being mixed with a polymeric agent (in general, a cationic polyelectrolyte chemical) and, secondly, being treated on centrifuging decanters to obtain a concentration in dried matter around 20-25%.

Bio-solids act accumulating substances and removing these ones from the original urban wastewater. There, our data [1,2] during 2001-2006, measured concentrations around 8% of total-N, around 4% in total-P, and important amounts of calcium, magnesium and potassium: this fact justifies the possible use of bio-solids derived from these wastewater in agriculture as fertilizers (composting or direct use).

On the other hand, in the above cited papers [1,2] we obtained rates of accumulation of substances in bio-solids from wastewater, expressed as the relation between concentration of any substance in the bio-solids (data over dried matter) and concentration in the raw wastewater original (mg/L). Thus, we concluded that organic matter (expressed as (BOD_5-COD)/2) and nitrogen were concentred around 300

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times, while phosphorous was concentred around 1,000 times.

With relation to metals [1,2], we obtained different accumulation coefficients in bio-solids: 1,100 times for iron, around 550 times to zinc and copper, 250 times to manganese, and coefficients lower for lead, chromium, nickel, mercury and cadmium.

Accumulation of metals in bio-solids must be generally influenced by the chemical behaviour of each metallic specie (i.e., redox state, complex formation, pH-reactions.), and by the dynamics of its adsorption or consumption by microorganisms present in wastewater [4-6]. These factors, very complex, have not been considered in the cited papers.

On the other hand, we must to get mention that the management of bio-solids generated in municipal wastewater treatment in the European Union is based in three items [7-9]: (i)reduction in generation [10], (ii)re-use [1,2,11,12], and (iii)treatment of bio-solids not managed as in (i) and (ii) [7-9,13].

The reduction in generation should imply a more exigent global dried process, with application of additional chemicals, which can suppose lower transportation costs of dried bio-solids due to a lower volume associated [13].

The re-use of bio-solids should imply two aspects: the agricultural use or the electric power production by anaerobic digesting of raw sludge. The agricultural use, direct or by composting [14], must have associated with a very strong control of industrial effluents discharged into public sewerage system: these practices should undoubtedly reduce the presence of metals, firstly in municipal wastewater and secondly, in the bio-solids generated in the WWTPs [4,6,15,16,26]. With respect to electric power production, the systems of co-generation are in progressive advance in the European Union.

Finally, other management processes of bio-solids can be the production of ceramics and building materials, and the energetic recuperation by means of pyrolization systems or gasification processes. In this case, the atmospheric emissions control will be critical [7,13,17,18].

On the other hand, application of bio-solids to agronomy is widely used in Spain, where are produced 701,751 T per year (data of 2018), being sent to agronomy the 85% [21]. If the bio-solids are destined to agronomy uses, levels of seven metals potentially present in bio-solids (Cd, Cu, Ni, Pb, Zn, Hg and Cr) must fit to the Spanish (and European) regulations applicable, and must always respect the parametric values established [14,20].

Taking into account the above said, the aim of this paper is to complete our investigations about the characterization of bio-solids produced in La Golondrina´s WWTP along 2000-2019, evaluating its compliance to Spanish normative for correct application in agronomy uses. Moreover, we will investigate rates of accumulation of pollutants from wastewater to bio-solids.

2. Materials and Methods

Methods used in characterization of wastewater were the conventional ones in this field [22-25]. Particularly, bio-chemical oxygen demand to 5 days (BOD_5) was measured by incubation in obscurity to 25ºC by using nitrification inhibitor (alil-thiourea), and chemical oxygen demand following the dichromate method.

Temperature, pH and conductivity were measured by using the common methods in wastewater analysis, while suspended solids used gravity methods [22-25]. Moreover, Cl, $SO_4^{=}$ and F^- were determined by ionic chromatography and cyanides by colorimetric determination.

Metals were determined by Inductive Coupled Plasma-Mass Spectrometry system. Nitrogen was determined according to Kjeldahl´s method and total phosphorous by ICP-SM after digesting the sample with ammonium persulfate in sulphuric medium.

Samples of both raw and treated wastewater were collected daily.

For ICP-SM measurements of metals existing in bio-solids, 1 g of dried bio-solids with 20 mL of distilled water, 3 mL of HCl and 1 mL of HNO_3 were digested during 2 h at 180ºC in a Teflon closed reactor, prior of ICP-SM analysis.

In this case, 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.

On the other hand, bio-solids were sampled monthly, during the first five days of each month.

3. Results and Discussion

Production and Characterization of raw wastewater and bio-solids: general aspects

La Golondrina´s WWTP is a conventional facility operated by activated sludges [1-4]. Treatment process carried out there 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, secondary settling and finally, disposal to Guadalquivir river. The plant can treat up to 145,000 m^3/day of municipal raw wastewater [27]. Moreover, from 2015 the treatment process in WWTP has been applied ferric or sulphate ferric as pre-treatment for an industrial effluent very few biodegrading received in plant and emanating from a yeast factory of the city.

Following with the description of WWWTP, tanks of biological treatment are equipped with anaerobic selection systems (24% of total volume of each aeration unit) to control the growth of filamentous bacteria in the treatment. The presence of these microorganisms could provoke serious problems in the secondary settling, with potential production of treated water of poor quality [1,3].

On the other hand, two gravity settlers concentrate primary sludges produced in primary settling and secondary sludges produced in secondary settling are concentrated by two flotation settlers (to obtain around 3-5% of dried matter in the two cases). Later, the two types of sludges are sent to temporary store units. Finally, the total sludges are dosed with a synthetic polymer to be dehydrated in two centrifuging decanters (to obtain around 20-25% of dried matter).

Summarizing, the WWTP produce treated wastewater according to the Spanish treatment normative which establish parametric values of 25 mg/L in BOD_5, 125 mg/L in COD, and 35 mg/L in suspended solids to treated wastewater in all the state. As we said above, the facility treats municipal wastewater from a Spanish middle city (actually, 327,000 h) with an industrialization degree of around 15%.

In this sense, Table 1 (a) shows mean values of characteristics investigated in raw wastewater along 2000-2019 as well as the average values of treated flows and dehydrated sludges production for the WWTP during the period studied (2000-2019) (Table 1 (b)). Generally, the production of bio-solids in wastewater treatment systems depends mainly on: (a)quantity of suspended solids in the raw water, and (b)organic load (BOD_5 or/and COD) present in wastewater influent to facility [10,17,19].

With respect to above Table 1 we can indicate that the amount of total heavy metals in raw wastewater was 1.104 mg/L, while the relation C/N/P, expressed as BOD_5/Kjeldahl-N/total-P was 359/55/5 whitin the range optimal to treat urban wastewater by biological conventional treatment [10,15,17].

At the same time, Fe was the majority metal present in wastewater, followed by Mn, Zn in Cu.

On the other hand, Table 2 shows the average values of all the studied parameters in the dehydrated sludges, that is, in bio-solids. We have investigated physical parameters, chemical ones, *salmonella* and *Escherichia coli*, and heavy metals and alkaline and alkaline-terrous metals: parameters determined in bio-solids are focused to its use in agronomy according the actual Spanish normative.

Table 1. (a)Characteristics of quality of raw wastewater of La Golondrina WWTP and (b)exploitation parameters and production of biosolids (2000-2019).

(a)

Parameter	Units	Mean Value
Temperature	*ºC*	*18.6*
pH	*Units of pH*	*7.55*
Conductivity	*microS/cm*	*918*
Suspended solids	*mg/L*	*319*
COD	*mg/L*	*591*
BOD_5	*mg/L*	*359*
Ammonium	*mg/L-NH_4*	*36.2*
Nitrates	*mg/L-NO_3*	*4.1*
Kjeldahl-N	*mg/L-NH_4*	*54.7*
Total-P	*mg/L-P*	*5.2*
Surfactants	*mg/L-LAS*	*6*
Oils and greases	*mg/L*	*73*
Chlorides	*mg/L*	*106*
Sulphates	*mg/L*	*89*
Fluorides	*mg/L*	*0.49*
Cyanides	*microg/L*	*<5*
Fe	*mg/L*	*0.620*
Mn	*mg/L*	*0.171*
As	*mg/L*	*0.007*
Pb	*mg/L*	*0.017*
Se	*mg/L*	*0.036*
Cu	*mg/L*	*0.091*
Zn	*mg/L*	*0.134*
Ni	*mg/L*	*0.008*
Cd	*mg/L*	*0.002*
Hg	*mg/L*	*0.013*
Cr	*mg/L*	*0.005*
Total coliforms	*Colony-forming units/L*	*$2.1x10^8$*
Escherichia coli	*Colony-forming units/L*	*$1.5x10^8$*

(b)	
Treated flow, m^3/year	*$26.55x10^6$*
Organic load, mg/L (*)	*475*
Suspended solids, mg/L	*319*
Biosolids, kg/year	*$38.00x10^6$*
kg biosolids per m^3/wastewater	*1.43*

(*)Organic load expressed as ([BOD_5+COD]/2).

Due to the specific situation of Spain about high production of bio-solids in their WWTP and need of high amounts of fertilizers to attend its agricultural production, Spanish have regulated since 1990 admissible characteristics in bio-solids for use in agronomy without affect negatively to soils.

In this sense, the first regulation, RD 1310/1990, [14] established restrictions to seven heavy metals of high pollutant power present potentially in bio-solids. The second regulation, O.M. AAA 1072/2013 [20], fixed the obligation to control several quality parameters (chemicals and micro-biologicals) of the bio-solids in order to control their quality, but without establish compliance values.

With relation to Table 2, in the drive columns we have included the two Spanish regulations applied to establish whether bio-solids can or not used for agronomy practices [14,20] commented above.

Table 2. Mean values of parameters studied in bio-solids (2000-2019) and Spanish normative applied to determine its use in agronomy.

Parameter	Units	Mean Value	Spanish Regulat.
Dryness	*% o.i.m.(1)*	*22.3*	(b)
Organic matter	*% o.d.m.(2)*	*74.9*	(b)
pH	*pH units*	*6.40*	(b)
Total-N	*% of N*	*6.6*	(b)
C/N	*Organic matter/ total N*	*16.4*	(b)
Ammonium-N	*% of NH_4(4)*	*5.0*	(b)
Total-P	*% of P_2O_5(4)*	*3.5*	(b)
K	*% of K_2O(4)*	*0.6*	(b)
Ca	*% of CaO(4)*	*3.7*	(b)
Mg	*% of MgO(4)*	*0.6*	(b)
Na	*% of Na(4)*	*0.1*	-
Fe	*mg/kg o.d.m.(3)*	*11,749.1*	(b)
Cu	*mg/kg o.d.m.(3)*	*392.8*	(a)
Mn	*mg/kg o.d.m.(3)*	*265.7*	-
Pb	*mg/kg o.d.m.(3)*	*64.3*	(a)
Cd	*mg/kg o.d.m.(3)*	*16.8*	(a)
Ni	*mg/kg o.d.m.(3)*	*21.6*	(a)
Cr	*mg/kg o.d.m.(3)*	*44.3*	(a)
Zn	*mg/kg o.d.m.(3)*	*463.1*	(a)
Hg	*mg/kg o.d.m.(3)*	*1.4*	(a)
As	*mg/kg o.d.m.(3)*	*8.5*	-
Se	*mg/kg o.d.m.(3)*	*5.7*	-
Co	*mg/kg o.d.m.(3)*	*4.0*	-
Salmonella	*Pres./Abs. per 25 g/bio-solids*	*Presence*	(b)
Escherichia coli	*Colony-forming units, per g/bio-solids*	*$4,1x10^8$*	(b)

(1)o.i.m.: over initial mass
(2)o.d.m.: over dried mass
(3)mg/kg o.d.m.: mg/kg over dried mass
(4)% of Ammonium, P, K, Ca, Mg and Na, over dried mass

(a)RD 1310/1990 (regulation translated from European Union)[14]
(b)O.M. AAA 1072/2013 [20]

As more information to respect, Spanish RD 1310/1990 [14] (Table 2, metals qualified with (a)) stablished maximum levels for only seven heavy metals in bio-solids to can be applied it to soils. These levels ensure that soils will not accumulate eventually toxic levels for their productive dynamics. Furthermore, parametric values of metals vary depending on pH of soils where are used: in acidic soils (pH<7) with higher mobility of metals, parametric values are lower than in basic soils (pH>7) with more low metallic mobility (Table 3).

Later, Spanish O.M. AAA 1072/2013 [20] marked the necessity to inform about several quality parameters of bio-solids, without to fix restrictions. This Spanish regulation translate the Directive 2008/98/CE of European Union to Spain. Due to that, analysis of *salmonella and Escherichia coli* in Table 2 corresponded to 2013-2019 period of our study.

Table 3. Heavy metals limited in agronomy use of bio-solids in Spain and parametric values (RD 1310/1990).

Metal	*Soils with pH<7*	*Soils with pH>7*
Cd, mg/kg o.d.m.	20	40
Cu, mg/kg o.d.m.	1,000	1,750
Ni, mg/kg o.d.m.	300	400
Pb, mg/kg o.d.m.	750	1,250
Zn, mg/kg o.d.m.	2,500	4,000
Hg, mg/kg o.d.m.	16	25
Cr, mg/kg o.d.m.	1,000	1,500

o.d.m.: over dried mass.

Dryness of bio-solids, Organic Matter, N and P

Figure 1 shows evolution between 2000-2019 of % total dried matter and % organic matter over dried matter of bio-solids investigated. Mean values of dried matter ranged between 20.1% and 25.8% with a mean value of 22.3%. Minimal values were founded in 2009 and 2012, and maximal values in 2010 and 2013.

With relation to organic matter over dried matter (Figure 2), evolution is approximately in opposite direction to above mentioned, with a mean value of 74.9%, and extreme values of 65.1% and 83.1%. Minimal values were found in 2001, 2007 and 2010, and maximum values corresponded to 2012,2015-2017 and 2019.

If we compare evolution of dried matter and that of organic matter, maximum values of the first one are frequently coincident with minimum values of the second ones: this can be explained taking into account that the lower values of dried matter the higher amount of water associated to bio-solids, and so, the lowest amount percentage of organic matter over the total of matrix.

On the other hand, we can observe in Figure 2 a slight but sustained increase in the value of % organic matter in bio-solids.

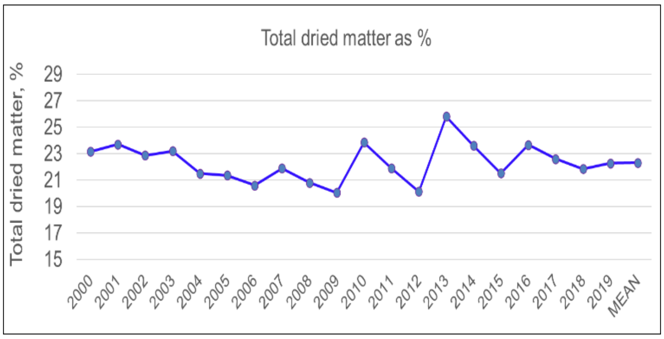

Figure 1. Evolution of dried matter in bio-solids (2000-2019).

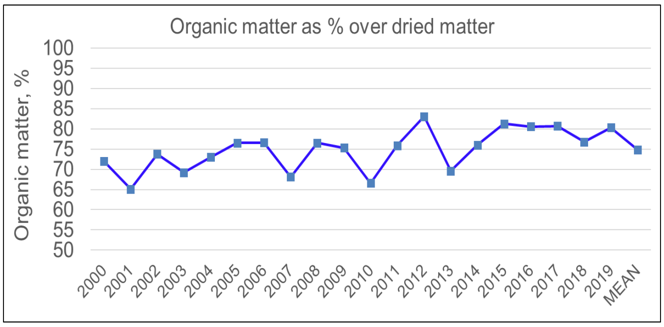

Figure 2. Evolution of organic matter over dried matter in bio-solids (2000-2019).

With respect to parameters of agronomic significance present in bio-solids, such as nitrogen (expressed as % Total-N o.d.m.), phosphorous (expressed as % Total-P_2O_5 o.d.m.) and potassium (expressed as % of K_2O o.d.m.), this evolution with time can be seen in Figure 3.

% Total-N ranged between 4.1% and 8.4% with a mean value of 6.6%. Minimum values corresponded to 2000, 2004, 2007 and 2019, while maximum values occurred during 2001-2003 and 2005 and 2014. Graph indicates relevant variations in amounts of N along the period investigated.

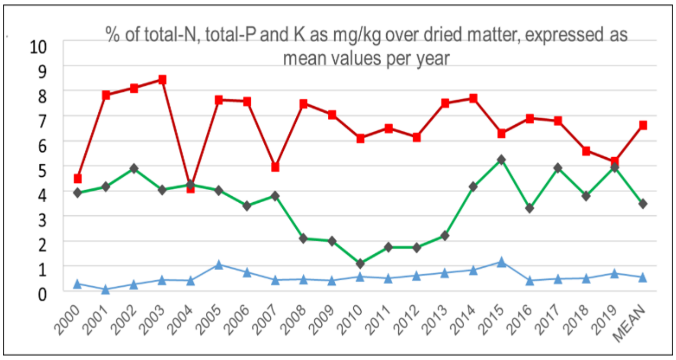

Figure 3. Evolution of N, P and K in bio-solids (2000-2019). Red squares, total-N; green squares, total-P; blue triangles, K.

On the other hand, % Total-P of bio-solids ranged between 1.1% and 5.3% with a mean value of 3.5%. Minimum values corresponded to 2008-2013 period, while maximum values occurred during 2002, 2015, 2017 and 2019. As in the above case of N, graph indicates relevant variations in levels of P along the period investigated. Data provided did not showed any clear correspondence between evolution of levels of N and P in bio-solids.

Finally, variations of K in bio-solids are moderate enough, exhibiting a mean value of 0.6% as K_2O and ranging between 0.1% and 1.2% as K_2O along the studied period.

Total heavy metals

Total concentration of heavy metals in bio-solids can be seen in Figure 4. Thus, the average of total concentration of metals along the checked period varied between 24,848 mg/kg o.d.m. in 2019 and 5,426 mg/kg o.d.m. in 2012, with a mean level of 13,024 mg/kg o.d.m.

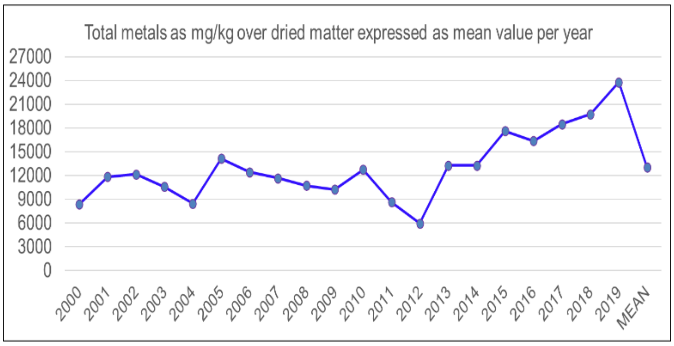

Figure 4. Evolution of concentration of total metals in bio-solids (2000-2019).

Graph indicates a clear increasing in total amount of metals, specially from 2015 to 2019. This behaviour can be explained by considering that since this year, we began the application of ferric chloride or sulphate to treat wastewater in our WWTP. Thus, amounts of Fe increased from 9.7 mg/kg o.d.m. (2000-2014, period) to 17.9 mg/kg o.d.m. (2015-2019, period), and consequently due to this question, total metals increased from 10.9 mg/kg o.d.m. up to 19.2 mg/kg o.d.m. in final bio-solids.

Summarizing: levels of the different materials found in bio-solids (organic matter, N, P, K, metals) vary with several factors that are very difficult to statistically control. In this way, we can cite: (a)flow of treated wastewater in plant, (b)rains which can modify the wastewater quality, (c)treatment effectively applied in the WWTP (reactants dosed if occurs), (d)system followed in the dried process of bio-solids (centrifuging, band filters), (e)use and dosage of polymers as aiding to dehydration and drying processes, and (f)time of storage of bio-solids after to be dried.

Due to above cited, our subject will not be to investigate all these aspects, but to have a quantitative approximation to know the final quality of bio-solids and its evolution with time; furthermore, whether bio-solids can or not used by agronomy applications according Spanish regulations.

In this way, the main metal present in bio-solids, Fe, is also the majority metal in original wastewater; its origin is double: raw urban wastewater, and specially, ferric salts used in the treatment of wastewater carried out in the WWTP. Likewise, Cu, Mn and Zn, the other majority metals in bio-solids, are also, majority metals in the original raw urban wastewater.

Moreover, the total sum of the seven metals included in the restrictions established to determine the use of bio-solids in agronomy was 991 mg/kg o.d.m. (mean value), ranging between a maximum of 2.108 and a minimum of 391 mg/kg o.d.m.

In this moment, we can follow evaluating the compliance of the seven heavy metals limited in the Spanish regulations to use in agronomy of bio-solids. This information is included in Table 4. It can be seen here that all the maximum values obtained for all the seven limited metals along the period 2000-2019 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.

Table 4. Metals limited to agronomy use of bio-solids in Spain and parametric values (RD 1310/1990).

Metal	Soils pH<7	Soils >7	Max. metal in biosolids
Cd, mg/kg o.d.m.	20	40	19
Cu, mg/kg o.d.m.	1,000	1,750	739
Ni, mg/kg o.d.m.	300	400	62
Pb, mg/kg o.d.m.	750	1,250	263
Zn, mg/kg o.d.m.	2,500	4,000	820
Hg, mg/kg o.d.m.	16	25	3
Cr, mg/kg o.d.m.	1,000	1,500	203

o.d.m.: over dried mass.

Metals with agronomy significance: Ca, Mg, K, Na

We can now consider the situation of alkaline and alkaline-terrous metals present in bio-solids. These metals are positive agronomy significance in the cases of Ca, K (above commented)and Mg, and on the contrary, can have negative influence, such as Na, because it could provoke salinization of soils and thus, affect negatively the cultures.

In Figure 5 it can be seen the evolution per years of the mean values corresponding to the sum of Ca, Mg, Na and K of bio-solids. Extreme values ranged between 3.2% and 7.4%, with a mean value of 5.0%. Maximun values were detected in 2005, 2015 and 2019, and the minimun ones occurred in 2007 and 2012.

We must note that the amount of 5.0% implies 50 g/kg, that is, 50,000 mg/kg o.d.m. as thus, a level much higher than associated to rest of metals above commented (with exception of Fe, above explained).

If we dissagregate the (Ca+Mg+K+Na) total values, the main metal was Ca with a mean value of 3.7% (2.1% maximum, 5.1% minimun): this suppose 37.000 mg/kg o.d.m. as CaO, with an important power as alkaline amendment of biosolids.

By considering the situation of K, its main value was 1.2% being 0.1% the minimun, and 0.6% the mean one. As above, this suppose 6.000 mg/kg o.d.m. as K_2O and a relevant power fertilizer of bio-solids.

Finally, we can indicate that the result for Mg was very similar to that of K (mean value 0.6%, maximum 1.1% and minimum 0,3%), and in the case of Na, the mean value was only 0.1%: thus, the affection over salinization of soils was not amountable.

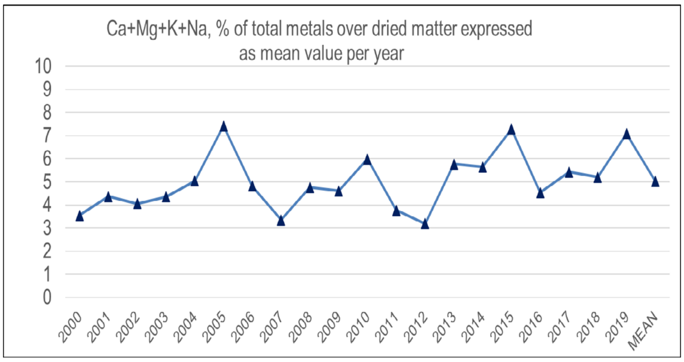

Figure 5. Evolution of total concentration of (Ca+Mg+K+Na) in bio-solids (2000-2019).

Bio-solids as container of matters and pollution of wastewater

In previous papers the role of biosolids acting as receiver of the pollution existing in wastewater was investigated [1,2]. To approximate us to this question we can compare the levels of different pollutants present in the original raw wastewater (metals, organic matter…) and the level of these pollutants in the final bio-solids produced in the WWTP. To obtain coherent data, let us consider that the density of wastewater is roughly the unity and 1 mg/L is equivalent to 1 mg/kg. Thus, we should compare the concentration of any pollutant in original wastewater as mg/L, and that of the same pollutant in final bio-solids as mg/kg (data over dried matter).

Firstly, above Table I already indicated that each cubic meter of wastewater influent to La Golondrina´s WWTP produces 1.43 kg of bio-solids (with 22.3% of dried matter). These dates are very similar to that of our above dates commented in the Introduction section (1.6 kg/m^3 and 21.9% of dryness).

All Wastewater Treatment Plants produce bio-solids integrated by dried matter and humidity (water) [6, 14, 26]. In this way, it could be more interesting to express the amount of substances in bio-solids over initial total matter than over dried matter. So, organic matter in bio-solids should correspond to:

74.9% x 0.223 = 16.70%, which expressed as mg/kg over initial matter ranges 167.000. If we make the approximation that mg/kg is equal to mg/L, result should be 167.000 mg/L of organic matter in bio-solids.

By considering the initial organic matter in raw wastewater (475 mg/L) and the final in bio-solids (167.000 mg/L) we can conclude that the rate of accumulation of organic matter from wastewater to bio-solid is 352 times. This value is also very similar that obtained for 2001-2006 (310 times).

With respect to the situation of nitrogen in bio-solids, its level was 6.6%, which expressed as mg/L over initial matter should be:

6.6% x 0.223 = 14,718 mg/L.

On the other hand, the concentration of N in wastewater was 54.7 mg/L as NH_4 which expressed as N ranges 42.5 mg/L. Thus, the rate of accumulation of N from wastewater to bio-solids should be 346. Again, this value is very similar to 311 obtained in 2001-2006.

If we repeat the calculation by P, we should obtain: P in wastewater, 5.2 mg/L. P in bio-solids, 3.5% x 0.223 as P_2O_5, and expressed as P, 335 mg/L. This result indicates a rate of accumulation of P from wastewater to bio-solids of 643.

In this case, coefficients of accumulation obtained now is lower than 1,070, this value obtained in 2001-2006 (but with the same order of magnitude). This can be consequence of a higher production of P associated to better behaviour of active sludges used to treatment in the WWTP against pollution received from 2007 to date [2].

In the case of heavy metals, we can calculate rates of accumulation for the seven metals included in the Spanish regulation to agronomy use. Table 5 shows results obtained.

Table 5. Rates of accumulation of metals limited for Spanish agronomy use, from wastewater to bio-solids.

Metal	Wastewater	Bio-solids	Ratio of Accumulation
Cd, mg/L	0.002	3.746	1,873
Cu, mg/L	0.091	87.594	962
Ni, mg/L	0.008	21.377	602
Pb, mg/L	0.017	14.339	843
Zn, mg/L	0.134	103.271	771
Hg, mg/L	0.013	0.312	24
Cr, mg/L	0.005	10.424	1,976

Metals more strongly accumulated in bio-solids are Cr, and Cd (>1,800 times), followed by Cu and Pb: all metals except Hg were accumulated more than 600 times from wastewater to bio-solids. In this way, is it known the possibility that Hg can scape to atmosphere since wastewater reducing thus its presence in bio-solids [10, 15, 17, 19].

These dates of accumulation of metals do not vary much with respect that obtained in 2001-2006, and moreover, both the concentration of all metals investigated in bio-solids (heavy+alkaline+alkaline-terrous) 13,024 mg/kg o.d.m., (11,115 mg/kg o.d.m. in 2001-2006) and rate of accumulation, 2,631 (2,434 obtained in 2001-2006) have been very close.

Finally, if we pay attention to microbiological aspect, we can observe that the level of *Escherichia coli* in wastewater ($1.5x10^8$ colony-forming units/L) changes very little with respect to bio-solids, $4.1x10^8$ colony-forming unit/g over total matter, or $0,9x10^8$ as dried matter. That is, the level of *Escherichia coli* even decreases by almost half from raw wastewater to bio-solids.

4. Conclusions

We carried out a survey about quality of bio-solids produced in a great Spanish Wastewater Treatment Plant during the last twenty years, because the important use in Spain of bio-solids generated in WWTP to agricultural practices. Our objective has been twofold: firstly, to check the quality and evolution in time of bio-solids from the point of view of their concentrations in organic matter, N, P, and both metals with agronomic significance and heavy metals. Secondly, to evaluate rates of accumulation of substances from raw wastewater to bio-solids. In this sense, the main conclusions extracted have been the following:

- Bio-solids represent an effective mechanism to remove pollution existing in urban wastewater and can be re-used as an effective fertilizer in agronomy.
- In this way, we have carried out an investigation over the production and characteristics of bio-solids produced in La Golondrina´s WWTP (Córdoba, Spain) along 2000-2019. This WWTP is a conventional facility operated by activated sludges which has treated a mean flow of $26.55x10^6$ m^3/year and has produced 1.43 kg of bio-solids per m^3 of treated wastewater.
- Bio-solids have shown a dryness over initial mass of 22.3%, and 74.9% of organic matter over dried matter. At the same time, major components of biosolids were N (as ammonium), P (as P_2O_5) and Ca (as CaO) which levels were 5.0%, 3.5% and 3.7%, respectively.
- On the other hand, total metals showed a concentration of 13,024 mg/kg over dried matter, being the main metal Fe, due to Fe was the majority metal in wastewater and, specially, to use of ferric chloride or sulphate in WWTP process. Other majority metals were Zn, Cu and Mn, with levels as mg/kg over dried mass of 463.1, 392.8 and 265.7, respectively. Rate of accumulation of total metals from wastewater to bio-solids was 2,632 times.
- As well and by considering the potential use of bio-solids in agronomy, the seven metals limited in Spanish regulations (Cd, Cu, Ni, Pb, An, Hg and Cr) exhibited concentration in bio-solids very lower than parametric values established. The metals more accumulated were Cr and Cu (>1,800 times), and the less, Hg (24 times).
- Finally, levels of *Escherichia coli* varied very little from wastewater to bio-solids: $1.5x10^8$ colony-forming units/L in the first, and $0.9x10^8$ colony-forming unit/g in the second, decreasing by almost half.

Declaration of Conflict of Interest

The author declares that there is no conflict of interest.

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