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Risk Assessment of the Use of Biosolids Containing Emerging Organic Contaminants in Agriculture

Paolo Roccaro*, Federico G. A. Vagliasindi

Department of Civil Engineering and Architecture, University of Catania, Viale A. Doria 6, 95125, Catania, Italy
proccaro@dica.unict.it

In this study the risk analysis related to the presence of selected pharmaceutical and personal care products (PPCPs) in biosolids used for land application was assessed. The target PPCPs (including antibiotics, antiepileptic, anti-depressant, and antibacterial) were selected based on the limited existing data on PPCPs occurrence in biosolids. The Environmental Protection Agency (EPA) Regulation (40 CFR Part 503) was adopted to carry out the risk analysis and the reference soil/biosolid concentration (RSC, mg of contaminant per kg of sludge) was calculated under different pathways. Obtained RSC values were compared with the concentrations of the target PPCPs observed in biosolids. It seems that the health risk related to the presence of the target PPCPs in biosolids is very low. However, due to the limited information on the effects of these and other emerging organic contaminants on the environment (e.g. toxicity, ecotoxicity, increased resistance of bacteria, possible synergistic effects due to the presence of emerging organic contaminants mixture) and because of the lack of information on their occurrence in biosolids, more research is needed to better ascertain the risk related to the land application of biosolids.

1. Introduction

Huge amounts (average 30 kg dry matter per inhabitant day) of sludge are generated all over the world from wastewater treatment plants (WWTPs). This results, for instance, in approximately 7 million dry tons of digested municipal sludge produced annually in the United States (NRC, 2002) and in 10 Mt dry in the European Member States (EU, 2002). The management of biosolids in an economically and environmentally acceptable way has become a matter of increasing importance during the last decades. While aerobic digestion is usually used for sludge stabilization, anaerobic digestion is commonly used at medium and large WWTPs. Land application of digested municipal sludge, also known as biosolids, is a possible alternative for reusing the biosolids instead of disposal which has risen significantly in the last decade. For instance, in Europe about 40 % of the produced biosolids are used in agriculture, while about 50% of the biosolids produced in US is applied to land as fertilizer or soil amendment. The rest is usually disposed in landfills or as landfill cover.

In the light of the increased production of sewage sludge across the European Union, the European Commission is currently considering whether the current Directive 86/278/EC (CEC, 1986) should be revised (EC, 2000). The regulation governing land application of sewage sludge in the United States was established by the Environmental Protection Agency (EPA) in 1993 in the Code of Federal Regulations, Title 40 (Part 503), under Section 405 (d) of the Clean Water Act (EPA, 1993). Nine inorganic chemicals in biosolids are currently regulated, and EPA is considering the addition of a class of organic chemicals (dioxins) to its regulation.

Biosolids are a complex mixture that contains several inorganic and organic contaminants of concern. While several studies have investigated the occurrence and health risk related to the heavy metals present in biosolids, limited information is available about the risk related to the presence of emerging organic contaminants, such as endocrine disrupting compounds (EDCs), pharmaceutical and personal care products (PPCPs) (Chaney et al., 1996; Duarte-Davidson and Jones, 1996; Rideout and Teschke, 2004). EDCs and PPCPs are emerging contaminants whose removal from wastewater can require advanced treatment processes with increasing treatment cost (Roccaro et al., 2013). EDCs and PPCPs are partially

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removed by the conventional biological processes (activated sludge) and they are also adsorbed in the sludge (Heidler and Halden, 2008). The occurrence of PPCPs in biosolids has been recently reported (Harrison et al., 2006; McClellan and Halden, 2009; Dìaz-Cruz et al. 2009; Walters et al. 2009). Therefore, in this study the risk analysis related to the land application of biosolids is carried out on selected PPCPs which were recently found in biosolids employing the EPA method (1995).

2. Materials and methods

The risk analysis for land application of biosolids containing PPCPs was conducted adopting the EPA Regulation (EPA, 1993). Table 1 shows the exposure pathways used in the risk analysis for land application of biosolids by the EPA (1995) and the related highly exposed individual (HEI). In this study, almost all the pathways which have the human as HEI (i.e. pathways 1, 3, 4, 5, and 12) were employed. Pathways 11 and 13 were not considered in this study because the target contaminants are not likely inhaled, while pathway 14 was not considered due to a lack of information on the migration of the target contaminants from soil to groundwater.
All the equations and values of parameters used in the following calculations are adopted from EPA (1995) if not specified.

Table 1: Exposure pathways used in risk analysis for land application of biosolids and related Highly Exposed Individual (EPA, 1995)

Pathway	Highly Exposed Individual (HEI)
1.Biosolids →Soil→Plant→Human	Human (except home garden) lifetime ingestion of plants grown in biosolids-amended soil
2. Biosolids →Soil→Plant→Human	Human (home garden) lifetime ingestion of plants grown in biosolids-amended soil
3.Biosolids →Human	Human (child) ingesting biosolids
4.Biosolids →Soil→ Plant→ Animal→Human	Human lifetime ingestion of animal products (animal raised on forage grown on biosolids-amended soil)
5.Biosolids →Soil→Animal→Human	Human lifetime ingestion of animal products (animal ingest biosolids directly
6.Biosolids →Soil→ Plant→ Animal	Animal lifetime ingestion of plants grown in biosolids-amended soil
7.Biosolids →Soil→Animal	Animal lifetime ingestion of biosolids
8.Biosolids →Soil→ Plant	Plant toxicity due to taking up biosolids pollutants when grown in biosolids-amended soil
9.Biosolids →Soil →Organism	Soil organism ingesting biosolids/soil mixture
10Biosolids →Soil →Organism →Organism→Predator	Predator of soil organisms that have been exposed to biosolids-amended soils
11Biosolids →Soil →Airborne Dust→Human	Adult human lifetime inhalation of particles (dust) (e.g., tractor driver tilling a field)
12.Biosolids →Soil →Surface Water→Human	Human lifetime drinking surface water and ingesting fish containing pollutants in biosolids
13.Biosolids →Soil →Air→Human	Human lifetime inhalation of pollutants in biosolids that volatilize to air
14.Biosolids →Soil →Ground Water→Human	Human lifetime drinking well water containing pollutants from biosolids that leached from soil to ground water

2.1 Pathway 1

For pathway 1, the adjusted reference intake of pollutant in human (RIA, µg/d) can be calculated using the following Eq(1).

$$RIA = \left(\frac{RfD \times BW}{RE} - TBI \right) \times 10^3 \quad (1)$$

with:

$$RfD = \frac{NOAEL\_or\_LOAEL}{(UF_1 \times UF_2 ...) \times MF} \quad (2)$$

where:

RfD = Oral reference dose (RfD values from Anderson et al. (2010) are reported in Table 2) - amount of intake of a non-carcinogenic pollutant without appreciable risk (mg/kg d);
NOAEL = No Observed Adverse Effect Level;
LOAEL = Lowest Observed Adverse Effect Level;
(UF1 x UF2…) = uncertainty factors;
MF = modification factor;
BW = body weight, assumed = 70 kg;
RE = relative effectiveness of ingestion exposure, assumed = 1;
TBI = total background intake rate from all sources, assumed = 0 mg/d.
The reference concentration of pollutant in soil (RLC, µg/g) was calculated with the following Eq(3):

$$RLC = \frac{RIA}{\sum UC \times DC \times FC} \quad (3)$$

with:
UC = plant uptake slope for pollutant from soils/biosolids, assumed = 0.001 (µg pollutant/g of dry plant tissue)/(kg pollutant/ha);
DC = dietary consumption of different food groups grown on land amended with biosolids, assumed = 125 (g/d);
FC = fraction of different group food groups assumed to be grown on land amended with biosolids, assumed = 0.25.
A first-order decay rate constant (k) was calculated by the following Eq (4) in order to take into account the degradation of the organic contaminant:

$$k = \frac{\ln 2}{T_{0.5}} \text{ (1/y)} \quad (4)$$

The calculated k values are reported in Table 2.
The reference annual application rate of pollutant (RP, kg/ha/y) was calculated using the following Eq (5):

$$RP = RLC \times MS \times 10^{-9} \times (1 + e^{-k} + e^{-2k} + e^{(1-n)k})^{-1} \quad (5)$$

with:
MS = assumed mass of dry soil in the upper 15 centimeters of soil (a $2x10^9$ g/ha);
n=number of years of application until equilibrium conditions reached.
Computed the RP value, the reference concentration of pollutant in biosolids (RSC, mg pollutant/kg biosolids DW) can be calculated using the following Eq (6).

$$RSC = \frac{RP}{AR \times 0.001} \quad (6)$$

with:
AR = annual whole biosolids application rate (10 t biosolids DW/ha/y);
0.001= conversion factor.

2.2 Pathway 3

For pathway 3, the RIA was calculated using Eq(1) and the RSC was computed with E(7).

$$RSC = \frac{RIA}{I_s \times DE} \quad (7)$$

with:
Is = biosolids ingestion rate by children, assumed = 0.2 (g/d);
DE = exposure duration adjustment, assumed = 0.0714 (used to take into account the fact that the RfD is derived for adult).

2.3 Pathway 4

For pathway 4, the RIA was calculated using Eq(1) and the reference concentration of pollutant in forage (RF, µg pollutant/g diet DW) was computed as following Eq(8):

$$RF = \frac{RIA}{\sum UA \times DA \times FA} \quad (8)$$

UA = animal tissue uptake slope (µg pollutant /g animal tissue)/(µg pollutant /g dry food);
DA = estimated lifetime average daily food intake, assumed = 57.37 (g/d);
FA = fraction of food group assumed to be derived from animals that ingest forage grown on biosolids-amended soil, assumed = 0.62.
UA values, assumed based on published data (Travi and Arms, 1988; EPA, 1995), are reported in Table 2.

In this case the RLC was calculated using Eq (9), while RP and RSC were calculated using Eq (5) and Eq (6), respectively.

$$RLC = \frac{RF}{UC} \tag{9}$$

2.4 Pathway 5

For pathway 5, the RSC is calculated using the following Eq (10).

$$RSC = \frac{RF}{FS} \tag{10}$$

with:
RF = see Eq. 8;
FS = fraction of animal diet which is biosolid, assumed = 0.015 (g biosolids DW/g diet DW).

2.5 Pathway 12

The reference water concentration for surface water (RCsw, mg/l) was calculated using the following Eq (11).

$$RC_{sw} = \frac{RfD \times BW}{(BCF \times FM \times P_f \times I_f) + I_w} \tag{11}$$

with:
BCF = pollutant-specific bioconcentration factor (L/kg);
FM = pollutant-specific food chain multiplier;
Pf = ratio of pollutant concentration in the edible portion of fish to concentration in whole fish, assumed = 0.5;
If = daily consumption of fish, assumed = 0.04 (kg/d);
Iw = daily consumption of water, assumed = 2 (kg/d).
BCF was calculated using the following Eq (12).

$$\log(BCF) = 0.79\log(Kow) - 0.4 - \log\left(\frac{7.6}{3}\right) \tag{12}$$

FM was calculated using the following Eq (13).

$$FM = 1 \rightarrow \log(kow) \leq 5; FM = 10 \rightarrow \log(kow) > 5 \tag{13}$$

The reference concentration of pollutant in eroded soil entering the stream (RCsed) was calculated using the following Eq (14).

$$RC_{sed} = RC_{sw}\left[KD_{sw} + \left(\frac{P_l}{P_s}\right)\left(\frac{1}{\rho}\right)\right] \tag{14}$$

with:
KDsw = partition coefficient between solids and liquids within the stream (L/kg);
Pl= percent liquid in the water column;
Ps = percent solids in the water column;
ρ = density of water, kg/L;
In particular, KDsw was determined following Eq(15).

$$KD_{sw} = Koc \times f_{oc} \tag{15}$$

with:
foc = fraction of organic carbon in soil, assumed = 0.01.
Koc derived from the following Eq(16).

$$\log(koc) = 0.0884 + 0.909\log(kow) \tag{16}$$

Based on the SMA (Sludge Management Area) defined by the EPA the following Eq (17) was used to calculate the reference pollutant concentration in soil eroding from the SMA (RCsma):

$$RC_{sma} = \frac{RC_{sed}}{DF} \tag{17}$$

with:
DF = dilution factor, assumed = 0.007.
The RP was then calculated with the following Eq (18).

$$RP = \frac{RC_{sma} \times ME_{sma}}{f_{ero}} \times 10^{-6} \tag{18}$$

with:

MEsma = estimated rate of soil loss for the SMA, assumed = 8400 (kg/ha/y);
fero = fraction of total loss caused by erosion, assumed = 0.033.
Using Eq (6) the RSC can be calculated from the RP.

3. Results and discussion

Obtained RSC values are reported in Table 2 which shows also the literature data on the occurrence of these PPCPs in biosolids, as maximum observed values. The comparison between the RSC values and the reported concentration in biosolids highlights that for these PPCPs the health risk due to land application of biosolids is very low. Indeed, there is at least a difference of three orders of magnitude between RSC values and actual concentrations of target PPCPs in biosolids. However, obtained results are based on input data, fate and transport models which are not exhaustive, therefore other studies are needed to better ascertain the risk related to the land application of biosolids containing these and other emerging contaminants. For instance, the potential health effects of drug resistant microbes need more research (Watkinson et al., 2007). The possible synergistic effects due to the presence of mixture of emerging organic contaminants needs to be evaluated. Further risk assessment may also be based on data concerning to long-term exposition (e.g. chronic toxicity tests or bioaccumulation study).

Table 2: Comparison between RSC values and maximum concentrations of target PPCPs in biosolids ([a]Anderson et al. (2010); [b]McClellan and Halden (2009); [c]Walters et al. (2009); [d]Dìaz-Cruz et al. (2009); N.A. = not available)

Contaminat	Limited pathway	RfD (mg/kg d)	K (1/y)	UA (µg pollutant /g animal tissue)/(µg pollutant /g dry food)	RSC (mg /kg DW)	Maximum concentration detected (mg /kg DW)
Chlortetracycline	5	30[a]	8.43	0.33	11,919	0.043[b]
Doxycycline	5	3[a]	2.11	0.52	754	1.780[b]
Erythromycin	5	5[a]	22	5.46	120	0.183[b]
Monensin	5	10[a]	12.65	33.27	39	N.A.
Oxytetracycline	5	30[a]	3.20	0.49	7,957	0.005[c]
Trimethoprim	5	4.20[a]	2.53	1.06	520	0.133[d]
Tilosyne	5	300[a]	31.6	1.84	21,441	0.005[c]
Carbamazapine	5	0.34[a]	3.37	3.43	13	0.238[b]
Fluoxetine	5	0.28[a]	2.11	2.43	15	0.258[b]
Triclosan	5	74[a]	2.11	20.58	472	1.508[d]

4. Conclusions

While several studies have investigated the occurrence and health risk related to the presence of heavy metals in biosolids, little information is available about the risk related to the presence of PPCPs, some of which are suspected EDCs. The occurrence of PPCPs in biosolids has been recently reported. Therefore, in this study the risk analysis related to the presence of selected PPCPs in biosolids was carried out. Obtained results showed that the use of biosolids containing the target PPCP for land application results in a low health risk. However, this study was limited to few PPCPs for which occurrence (in biosolids) and toxicity data are available. Therefore, due to the limited information on the fate and effects of these and other emerging organic contaminants in the environment (e.g. toxicity, ecotoxicity, increased resistance of bacteria, possible synergistic effects due to the presence of emerging organic contaminants mixture) more research is needed to better ascertain the risk related to the land application of biosolids. A holistic approach based on the comprehensive evaluation of emerging contaminant from source to sink is needed in order to identify the sustainable solution for minimizing and controlling the risk related their presence in the environmental matrices, overcoming the current risk assessment approach which is based on the study of selected pollutants in a single matrix (e.g. water, biosolids, air).

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