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Scientific basis of dissolved organic carbon limitation for landfilling of municipal treatment sludge – Is it attainable and justifiable?

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ABSTRACT

This study evaluated the scientific and technical basis of the dissolved organic carbon (DOC) limitation imposed on municipal sludge for landfilling, mainly for assessing the attainability of the implemented numerical level. For this purpose, related conceptual framework was analyzed, covering related sewage characteristics, soluble microbial products generation, and substrate solubilization and leakage due to hydrolysis. Soluble COD footprint was experimentally established for a selected treatment plant, including all the key steps in the sequence of wastewater treatment and sludge handling. Observed results were compared with reported DOCs in other treatment configurations. None of the leakage tests performed or considered in the study could even come close to the prescribed limitation. All observed results reflected 10–20 fold higher DOC levels than the numerical limit of 800 mg/kg (80 mg/L), providing conclusive evidence that the DOC limitation imposed on municipal treatment sludge for landfilling is not attainable, and therefore not justifiable on the basis of currently available technology.

1. Introduction

Municipal sludge, a major by-product of treatment processes, originates from the treatment of domestic sewage. Essentially, it consists of viable and non-viable organic matter, also rich in nutrients. Its composition largely depends upon the adopted configuration of the treatment scheme. While biological treatment is a prerequisite for domestic sewage in meeting the effluent requirements, it may be implemented in different ways with and without primary settling. The primary sludge – i.e., solids separated by means of primary settling – basically includes settleable inorganic and organic pollutants in the sewage stream (Cokgor et al., 2009; Ucisik and Henze, 2008), whereas the secondary sludge (excess solids from biological processes) mainly contains viable biomass together with entrapped endogenous residues and non-biodegradable particulate pollutants (Yuan et al., 2013). Furthermore, the sludge composition is largely affected by the way the biological units are designed and operated. The sludge age changes the stabilization properties of the sludge (Cokgor et al., 2012; Xiong et al., 2012; Yuan et al., 2009). The sludge generated from biological treatment systems designed for organic carbon or nutrient removal may have significantly different properties (Henze et al., 1998; Kelessidis and Stasinakis, 2012).

Until recently, sludge disposal has attracted little attention compared with considerable emphasis on discharges of treated wastewaters. With the new conceptual approach regarding waste as a resource and encouraging recycle and reuse especially in the EU countries, a different sludge management scheme has emerged with a number of applicable pre-treatment, reuse and final disposal options (Donovan et al., 2010). These options generally include energy-based alternatives such as gasification, incineration or usage as supplementary fuel for industrial plants and also land-based alternatives involving reuse in agriculture and reclamation, compositing, all contrasted with basic landfilling (Mills et al., 2014; Spinosa et al., 2011).

Each of these management options has its own merits and disadvantages. While detailed appraisal of available alternatives is beyond the scope of the study, it should be stated that there is

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Nomenclature

b_H	rate coefficient for endogenous decay (1/d)
CAS	conventional activated sludge system
COD	chemical oxygen demand
C_S	total biodegradable COD concentration (mg/L)
C_T	total COD concentration of the wastewater (mg/L)
C_{T0}	total COD concentration in the influent (mg/L)
DOC	dissolved organic carbon
DOC_{ET}	final soluble DOC concentration of the eluate test (mg/L)
DOC_{ET1}	initial soluble DOC concentration of the eluate test (mg/L)
DR	dry matter content ratio (%)
EU	European Union
f_{ES}	the fraction of the endogenous biomass converted into soluble inert products
k_h	hydrolysis rate (1/d)
L	leachant
L/S	liquid to solid
MC	moisture content of the undried sludge sample (%)
M_D	mass of dry sludge (kg)
M_W	mass of undried sample (kg)
P_{PS}	primary sludge generation (kg SS/d)
P_{XE}	the amount of sludge from endogenous particulate matter (kg cell COD/d)
P_{XH}	the daily generation of active heterotrophic biomass (kg cell COD/d)
P_{XHE}	excess sludge production through generation of active and endogenous biomass (kg cell COD/d)
P_{XI}	the amount of sludge from inert particulate COD (kg cell COD/d)
P_{XT}	total daily excess sludge (kg cell COD/d)
S_E	soluble COD concentration in the effluent of secondary settling tank (mg/L)
S_{ET1}	initial soluble COD concentration of the eluate test (mg/L)
S_I	soluble inert COD content of the wastewater (mg/L)
SMP	soluble microbial products
S_P	soluble microbial product concentration (mg/L)
S_R	the total soluble residual COD in the effluent (mg/L)
SS	suspended solids (mg/L)
S_T	the total soluble COD content of the wastewater (mg/L)
S_{T0}	soluble COD concentration in the influent (mg/L)
S_{T1}	soluble COD concentration of the primary sludge (mg/L)
S_{T2}	soluble COD concentration of the secondary sludge (mg/L)
S_{T3}	soluble COD concentration in the influent of the anaerobic digester (mg/L)
S_{T4}	soluble COD concentration in the effluent of the anaerobic digester (mg/L)
S_{TE}	final soluble COD concentration of the eluate test (mg/L)
TDS	total dissolved solids (mg/L)
V_{PS}	volume of primary sludge (m^3/d)
VSS	volatile suspended solids (mg/L)
X_E	particulate inert endogenous products (mg cell COD/L)
X_H	active heterotrophic biomass concentration (mg cell-COD/L)
X_I	influent particulate COD (mg COD/L)
X_T	total sludge concentration (mg VSS/L)
Y_H	yield coefficient for heterotrophic biomass (mg cell-COD/mg COD)
Y_{NH}	net yield coefficient (mg cell COD/mg COD)
Y_{SP}	yield coefficient for soluble residual products (mg COD/mg COD)
θ_X	sludge age (d)

now a tendency to consider re-use in agriculture as the primary beneficial route for municipal sludge (Lederer and Rechberger, 2010). However, this approach needs careful evaluation from different perspectives. First of all, municipal sludge would also contain heavy metals, non-biodegradable harmful chemicals and potentially pathogenic microorganisms, all likely to create serious health concerns in the long run (Astals et al., 2013; Horn et al., 2003; Hospido et al., 2010; Lozano Sandoval et al., 2009; Snyder and O'Connor, 2013). In this context, sludge use in agriculture may become the most sensitive of disposal routes in view of the fact that it is the one over which water authorities have the least control. Secondly, aside from potential health risks of sludge reuse as an alternative to the artificial fertilizer, agricultural market has to be developed and the product acceptance should be achieved. Untreated sewage has a poor image, which must be overcome before the acceptance of agricultural use. It should be recognized that the agricultural outlet is still vulnerable to adverse publicity. For agricultural use, characteristics and area of available land may also pose major constraints. Therefore, a management plan primarily involving re-use in agriculture, also requires an auxiliary/transition plan for safe disposal of sludge: This is definitely landfilling.

Despite EU efforts toward its minimization, landfilling is still the widest implemented method for the final disposal of municipal sludge. Similar to some EU countries, more than 50% of municipal sludge produced in Turkey goes to landfill sites (Kelessidis and Stasinakis, 2012; O'Donovan and Barry, 2012). With the expected increase in sludge production, landfilling will still be the most applied disposal method as there are no feasible alternatives with such high capacity.

EU regulations seek to minimize landfilling. In fact, the purpose of the directive on the landfill of waste, 99/31/EC (Council Directive, 1999) is to minimize the role and magnitude of landfill in waste management/recovery sector. The directive intends to prevent and reduce the adverse effect of waste landfilling on the environment. One of the most controversial limitations imposed by the directive is the limit of 80 mg/L for the dissolved organic carbon (DOC) parameter in the leachate based on eluate test. Numerous studies conducted on sludge generated from municipal treatment plants have clearly indicated that observed DOC levels largely exceed this limit, regardless of the characteristics and the stability of the sludge (Pehlivanoglu-Mantas et al., 2007; Spinosa et al., 2011; Wasterhoff and Pinney, 2000; Zhang et al., 2009).

In this context, the objective of the study was to evaluate the scientific and technical basis of the DOC limitation imposed on municipal sludge for landfilling. The evaluation primarily explored whether the DOC limit can possibly be achieved by means of available treatment technologies and if not, is it justifiable to use this numerical limit as a regulatory constraint, which will totally prohibit the landfilling application, rather than presumably reducing its likely adverse effects.

1.1. Legislative framework

EU directives provide the relevant legislative basis concerning the DOC limitations for considering landfilling as the ultimate disposal option for municipal sludge. In this context, five different directives or council decisions may be cited:

Sewage Sludge Directive, 86/278/EEC (Council Directive, 1986) – This early directive sets the basis for significant characteristics of sludge as related to disposal alternatives. It seeks to encourage the use of sewage sludge in agriculture and to regulate its use in such a way as to prevent harmful effects on soil, vegetation, animals and man. Since its promulgation, many countries have started to implement stricter regulations. Some countries have already included limit values for organic micro-pollutants, which are not yet required by the current legislation.

Waste Landfill Directive, 1999/31/EC (Council Directive, 1999) – This directive, while defining the permissible basis for landfilling of sludge, intends more to prevent adverse effects of landfilling on the environment, in particular on the surface and ground water, soil, air and human health, i.e., decrease in methane generation, reduction of the quantity and toxicity of leachate from the landfill sites. In essence, the real objective of the directive appears to minimize the role of landfilling in the waste recovery sector. Similarly, the following *Council Directive 1999/31/EC*, while expanding on safe and controlled landfill activities in the EU, underlines that prevention, recycling and recovery of waste should be encouraged as should the use of recovered materials and energy, so as to safeguard natural resources and obviate wasteful use of land. Furthermore, it indicates that further consideration should be given to issues of incineration, compositing, biomethanisation. It also provides a technical basis for testing and acceptance of wastes at three different levels: Level 1 – basic characterization, basically short and long term leaching behavior; level 2 – compliance testing, whether the waste complies with permit conditions and level 3 – on-site verification.

Decision on Hazardous Waste, 2000/532/EC (Commission Decision, 2000) – This legislative document is extremely important, mainly because it classifies municipal sludge as a *non-hazardous waste* i.e., section 19 06 01: anaerobic treatment sludges of municipal and similar wastes, section 19 08 05: sludge from treatment of urban wastewater.

Finally, *Decision establishing criteria and procedures for the acceptance of waste at landfills*, 2003/33/EC (Council Decision, 2003) – This document gives description of procedures, limit values and other criteria for accepting waste at different classes of landfill sites. Specifically, Section 2.2.2 of the Council document defines limits of acceptance for non-hazardous wastes into landfills. The list includes heavy metals, TDS and specifically chloride, fluoride and sulfate and a DOC limit of 800 mg/kg as dry matter.

2. Materials and methods

2.1. Rationale for evaluation

The evaluation concerning the scientific and practical value of the DOC limitations imposed by European directives for landfilling primarily relied upon (i) a review of the theoretical basis for the expected DOC footprint through a process flow scheme commonly adopted for municipal wastewater and sludge treatment. (ii) Experimental assessment of the same DOC footprint in a selected plant treating domestic sewage.

For this purpose, the treatment plant serving one of the largest towns in *Central Anatolia, Turkey*, with a population of around 650,000, was selected for experimental evaluation of the observed soluble COD and DOC footprints. The plant involved two parallel modules, each including a sequence of preliminary treatment units – screens and grit removal – primary settling; activated sludge unit with aeration tank and secondary settling prior to treated effluent discharge for the wastewater stream. Similarly, the corresponding sludge processing stream was composed of gravity thickening for primary sludge; drum thickening of the secondary sludge; anaerobic digestion of combined sludge with a hydraulic retention time (HRT) of sixteen days and dewatering of the digested sludge by centrifuge/decanter to around 23% dry matter content, to be evaluated by the eluate test for appropriate final disposal. The plant performance was monitored for a period of 6 months on a daily basis, basically to follow the fate of soluble COD, together with all related parameters, through different key steps of liquid and solid waste streams.

2.2. The eluate method

The methodology relies on the measurement of leachate from a sludge sample with a liquid to solid (L/S) ratio of 10 L/1.0 kg (EN 12457-4, 2002). The procedure requires placing a test sample of 0.090 kg of dry sludge (M_D) in a bottle yielding a total mass of M_W and taking into account the dry matter content ratio (DR) of the sludge sample. The critical point for a reliable result is to sustain the experimental conditions defined in the reference document, which relies on the proper assessment of dry matter content.

The amount of undried sample (M_W) to be tested is determined with the following expression:

$$M_W = M_D/DR \times 100 \tag{1}$$

In order to attain an L/S ratio of 10 L/1.0 kg, first the moisture content of the undried sludge sample (MC) is determined by using the following expression:

$$MC = 100 \times (M_W - M_D)/M_D \tag{2}$$

The required leachant (L) amount to end up with a ratio of 10 L/1.0 kg, is determined by using the following expression:

$$L = (10 - MC/100) \times M_D \tag{3}$$

The whole content of the mixture is agitated for 24 h by using an agitation device and the filtrate from 0.45 μm filter is analyzed for different parameters as given in the Regulation for Waste Landfill (Council Decision, 2003) (see Fig. 1).

2.3. Analytical methods

Suspended solids (SS) and volatile suspended solids (VSS) parameters were determined according to Standard Methods (Standard Methods, 2005). COD measurement was accomplished following the procedure defined by ISO 6060 (ISO, 1989). DOC was measured using high temperature combustion using a Shimadzu TOC-5000A analyzer (Shimadzu Corporation, Kyoto, Japan) according to Turkish Standards – TS 8195 EN 1484 (TSE, 2000).

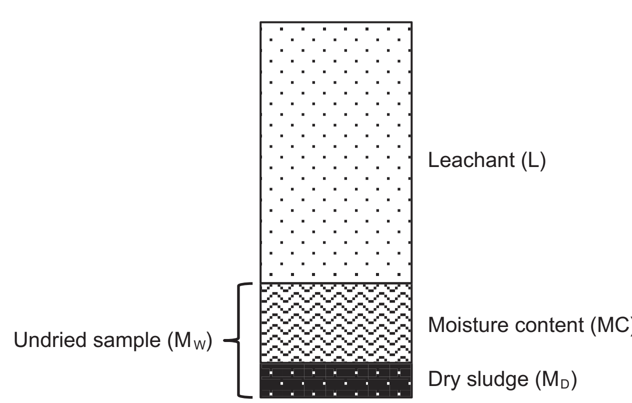

Fig. 1. Physical characteristics of the eluate test.

3. Theory and calculation

Conceptual evaluation of the DOC/soluble COD footprint within a treatment plant should primarily consider relevant characteristics of domestic sewage, together with related biochemical mechanisms contributing to the generation and leakage of soluble COD/DOC from sludge at different steps of the treatment sequence before the eluate test and final disposal. Hydrolysis, endogenous respiration and generation of soluble microbial products should be recognized as major components of the complex array of interacting biochemical mechanisms, all ending with DOC leakage.

3.1. Related sewage characteristics

Expected results of the DOC leakage test applied to sludge would be primarily related to the magnitude and fate of organics in domestic sewage, mainly because (i) the water content of the sludge will entrain the residual soluble COD in the treatment units and (ii) the leakage potential of the sludge will depend on the characteristics of the treated wastewater. In this context, the total soluble COD (S_T) and soluble inert COD (S_I) content of the wastewater as well as the level of soluble microbial products (S_P) likely to be released as part of biochemical reactions should be primarily considered for this evaluation.

Both S_T and S_I are generally defined as fractions of the total COD concentration, C_T characterizing domestic sewage. Okutman Tas et al. (2009) reported C_T range of 340–680 mg/L for six different sewage discharges in Istanbul and compared them with a similar C_T range of 233–634 mg/L characterizing seven different countries in Europe and they calculated an average S_T/C_T ratio of 29%, based on an average S_T level of 132 mg/L. This level was in agreement with the results of an earlier study conducted on 13 different sewage stations associated with C_T and S_T ranges between 315–840 mg/L and 125–240 mg/L, respectively; the average values characterizing these range were 605 mg/L for C_T and 190 mg/L for S_T, corresponding of the S_T/C_T ratio of 32% (Orhon et al., 1997). An earlier study related to the nitrification/denitrification potential of sewage also yielded 170 mg/L for S_T, but a slightly higher S_T/C_T ratio of 39%, due to lower average total COD content of sewage at the selected site (Isabel Pelaez et al., 2009; Orhon et al., 1994).

A number of similar researches were also devoted to the assessment of initial inert COD in sewage. In 16 different surveys on domestic sewage from six different countries where C_T varied between 220 and 530 mg/L, the initial soluble inert fraction, S_I was calculated to remain in the range of 2–20% of the total COD, with an average S_I/C_T ratio of 8.7%. Similarly, an average ratio of 14.6% was suggested for the particulate inert COD fraction, X_I, within a range of 4–25% (de la Sota et al., 1994; Ekama et al., 1986; Henze, 1992; Henze et al., 1987; Kappeler and Gujer, 1992; Sollfrank et al., 1992). In Turkey, lower values for both S_I and X_I were found to characterize domestic wastewater: A survey on four different domestic wastewaters with average C_T levels between 315 and 630 mg/L, indicated an S_I range of 16–56 mg/L with an average S_I/C_T ratio of 4%; the corresponding average X_I/C_T ratio was also reported as 10% (Orhon and Cokgor, 1997). Also, a recent study on gray and black water fractions of domestic wastewater yielded an S_I/C_T ratio of 3.7% for *black water* (C_T = 1145 mg/L), 5% in *gray water* (C_T = 275 mg/L) and 4.5% in combined wastewater (Hocaoglu et al., 2010).

3.2. Concept of soluble microbial products

Treatment sludge mainly contains active biomass and COD/DOC generation is essentially related to metabolic activities of the microbial population in the sludge. A number of different mechanisms such as disintegration, hydrolysis, decay and lysis, and endogenous decay, may be envisaged (Ni et al., 2011) to explain soluble COD generation. However, in the context of aerobic processes related to biological wastewater treatment, one of the major mechanisms is the generation and leakage of soluble microbial products from biomass.

The concept of soluble microbial products has been well studied and reported in the literature (Barker and Stuckey, 1999). Experimental proof on the existence and significance of SMPs in microbial cultures sustained in biological treatment systems has been provided since 1961 (Artan and Orhon, 1989; Chudoba et al., 1968; Gaffney and Heukelekian, 1961; Hejzlar and Chudoba, 1986). Originally, in a study on the biodegradation of acetate at high concentrations, Gaffney and Heukelekian (1961) showed that a residual COD remained in filtered mixed liquor samples after complete removal of available acetate; the level of the residual COD was found to be around 10% of the initial acetate COD. The nature of SMPs is still not well understood. Some studies claim that they are biodegradable (Daigger and Grady, 1977; Rittmann et al., 1987). Others argue that they are non-biodegradable. In essence, a portion of SMPs may undergo biodegradation, but at such a slow rate that they may be considered residual and remain accumulated in biological reactors (Gaudy and Blachly, 1985; Orhon et al., 1989; Orhon and Okutman, 2003).

The mechanism for the generation and accumulation of SMPs depends on the adopted modeling approach: Growth-associated formation of SMPs stipulates that a fraction of the incoming substrate is directly converted into residual soluble microbial products. Conversely, a decay-associated mechanism of SMP generation assumes that a fraction of endogenous residues generated during endogenous respiration and decay is soluble residual organics released back to the reactor volume. The basic rate expression for the generation of SMPs through microbial decay is generally defined as follows (Orhon et al., 2009):

$$\frac{dS_p}{dt} = f_{ES} \cdot b_H \cdot X_H \tag{4}$$

where S_P is the concentration of residual soluble microbial products; f_{ES} is the soluble residual fraction of endogenous residue; b_H is the rate coefficient for endogenous decay and X_H is the active heterotrophic biomass concentration.

Based on the process stoichiometry and mass balance, the magnitude of S_P can also be approximated as a function of the total biodegradable COD (C_S) in relation of metabolic reactions taking place in the biological treatment systems (Orhon et al., 1999):

$$S_P = Y_{SP} \cdot C_S \tag{5}$$

where

$$Y_{SP} = f_{ES} \cdot Y_H \tag{6}$$

and, Y_{SP} is the coefficient for soluble residual products; C_S is the total biodegradable COD concentration in the process influent; Y_H is the heterotrophic yield coefficient. Different studies conducted on domestic sewage reported Y_{SP} values in the range of 0.061–0.096 mg COD/mg COD. Using the commonly accepted value of 0.64 mg cell COD/mg COD for Y_H, the corresponding f_{ES} can be placed within the bracket of 0.08–0.14 (Germirli et al., 1998; Lesouef et al., 1992; Orhon and Cokgor, 1997; Pala-Ozkok et al., 2013).

3.3. Conceptual DOC footprint

A conceptual soluble COD/DOC footprint may be assessed based on mass balance implemented to the sequence of wastewater treatment units. In the context of available information on the

Table 1
Adopted sewage characteristics for DOC footprint.

Parameter	Adopted value
C_T (mg COD/L)	550
X_{SS} (mg SS/L)	350
S_T (mg COD/L)	170
C_S (mg COD/L)	450
S_I (mg COD/L)	34
X_I (mg COD/L)	66
Y_H (mg cell COD/mg COD)	0.64
Y_{SP} (mg cell COD/mg COD)	0.06
b_H (d^{-1})	0.20
f_{ES}	0.10
f_{EX}	0.20
$i_{SS,COD}$ (mg SS/mg COD)	0.90

biodegradation properties of domestic sewage, typical characteristics applicable to a general mass balance evaluation are outlined in Table 1. The table essentially defines a domestic sewage with a total COD concentration, C_T of 550 mg/L and a suspended solids concentration, X_{SS} of 350 mg/L. A conventional activated sludge system (CAS) operated for organic carbon removal from domestic sewage generally involves a *primary sludge,* P_{PS} generated by primary settling and a *biological* or *secondary sludge,* P_{XT}, which is essentially excess biomass, extracted from secondary settling tanks. CAS may also be operated without primary settling, as an extended aeration process modification or in order to balance the necessary carbon to nitrogen (C/N) ratio in nutrient removal systems (Pincince et al., 1997).

Fig. 2 illustrates the basic mass balance around the primary settling tank of a CAS system based on characteristics given in Table 1 and operated for organic carbon removal for simplicity of evaluation. Mass balance was established for a conceptual sewage flow rate of 1000 m^3/d, adopting generally reported settling efficiencies of 67% (60–70%) for suspended solids and 33% (30–40%) for COD in this unit (EPA, 1997); a 50% removal of influent particulate inert COD, X_I was accepted using the reported experimental data of Okutman Tas et al. (2009). As illustrated in Fig. 2, mass balance yielded a P_{PS} level of 235 kg SS/d (235 kg SS/1000 m^3), corresponding to a primary sludge volume, V_{PS} of 11.75 m^3/d based on a 2% dry matter content (DM) in settled sludge. The important part of the mass balance is the fact that the soluble COD concentration of the aqueous phase of the primary sludge will be the same as that of domestic sewage. In simpler words, the primary sludge will contain a soluble COD content of 170 mg/L, as in raw sewage.

A similar mass balance is also illustrated in Fig. 3, for the biological sludge generation in the same CAS system. Relevant

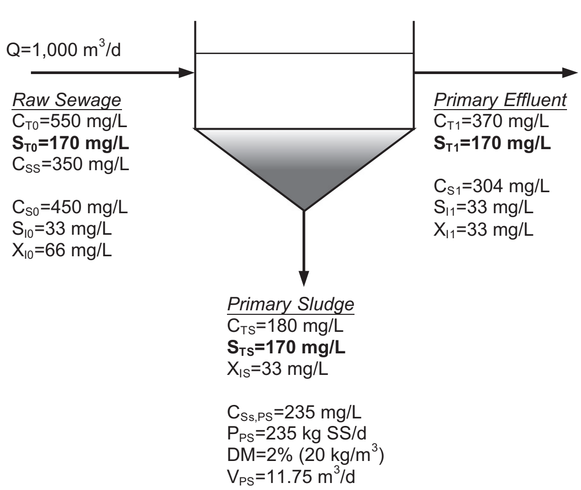

Fig. 2. COD mass balance in primary settling tank.

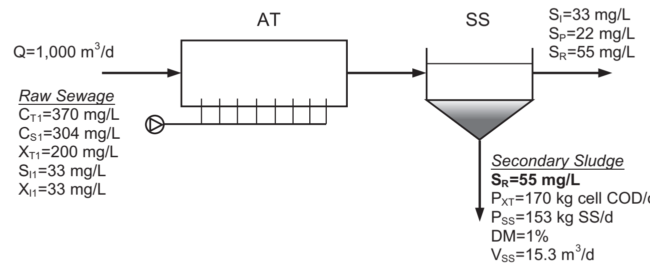

Fig. 3. COD mass balance in secondary settling.

calculations were made for a selected sludge age, θ_X value of 6 d; They were based upon the following expressions defining the net yield coefficient, Y_{NH}, and the secondary sludge components, P_{XH}, P_{XE} and P_{XI} corresponding to relative contributions of active biomass, X_H, endogenous particulate matter, X_E and influent inert particulate COD, X_I respectively. These mass balance expressions are described in detail in the literature (Orhon and Artan, 1994; Orhon et al., 2009):

$$Y_{NH} = \frac{Y_H}{1 + b_H \cdot \theta_X} = \frac{0.64}{1 + 0.2 \cdot 6} = 0.30 \text{ mg cell COD/mg COD} \tag{7}$$

$$P_{XH} = Q \cdot C_{S1} \cdot Y_{NH} = 1000 \cdot 0.304 \cdot 0.3 = 91 \text{ kg cell COD/d} \tag{8}$$

$$P_{XHE} = P_{XH} + P_{XE} = P_{XH}(1 + f_{EX} \cdot b_H \cdot \theta_X) = 113 \text{ kg cell COD/d} \tag{9}$$

where P_{XHE} excess sludge production through generation of active and endogenous biomass fraction.

$$P_{XI} = 1000 \cdot 0.03 = 33 \text{ kg cell COD/d} \tag{10}$$

$$P_{XT} = P_{XHE} + P_{XI} = P_{XH} + P_{XE} + P_{XI} = 113 + 33 = 146 \text{ kg cell COD/d} \tag{11}$$

As shown above, calculations based on the adopted characteristics yielded a total secondary sludge, P_{XT}, amount of 146 kg cell - COD/d, where P_{XH} = 91 kg cell COD/d, P_{XE} = 22 kg cell COD/d and P_{XI} = 33 kg cell COD/d. Using the commonly accepted conversion factor $i_{SS,COD}$ of 0.9 kg SS/kg COD (Gujer et al., 2000), the total secondary sludge, P_{SS} could be computed as 131 kg SS/d. Adopting an average dry matter content of 1% (10,000 mg/L), the corresponding secondary sludge volume, V_{SS} was determined as 13.1 m^3/d. This way, mass balance indicated a total sludge volume of 25 m^3/d with 47% primary sludge and 53% secondary sludge.

It is usually argued that CAS is over-designed for substrate removal, depleting all biodegradable COD available in the influent, so that the effluent soluble COD is essentially composed of inert soluble COD of influent origin, S_I together with soluble microbial products, S_P generated in the course of biochemical reactions (Germirli et al., 1991). For the selected wastewater characteristics S_I is 33 mg/L and S_P could be calculated as 18 mg/L from Eq. (5), yielding the total soluble residual COD in the effluent, S_R as 51 mg/L. The same S_R level is also incorporated in the aqueous phase of the secondary sludge.

In the treatment plant, primary sludge and secondary sludge are combined and homogenized before further processing. The soluble COD content of the homogenized total sludge was calculated approximately as 105 mg/L from simple mass balance. In the leaching test, the soluble organic content of sludge is evaluated in terms of DOC parameter. Very few studies involve simultaneous COD and DOC measurements in sewage: Katsoyianis and Samara (2007) reported only an average DOC value of 72 mg/L for raw sewage and 19 mg/L for secondary effluent; Dignac et al. (2000) obtained average values of 300 mg/L and 82 mg/L for soluble COD and DOC in wastewater, corresponding to a COD/DOC ratio of 3.64. In a survey conducted at one of the largest treatment plants in Istanbul, Turkey, for 6 months in 2007, influent soluble COD, S_T and DOC were observed to vary between 220–275 mg/L and 72–80 mg/L respectively, corresponding to a S_T/DOC ratio of 3.1 ± 0.25 (Pehlivanoğlu-Mantas et al., 2007). Theoretical COD/DOC ratios may be calculated as 2.67 for carbohydrates and biomass. Consequently, assuming an overall soluble COD/DOC ratio of 3.0 for the above mass balance evaluations, the level of 105 mg/L of soluble COD derived from mass balance for the mixed (primary + secondary) sludge corresponds to a DOC value of 35 mg/L.

3.4. Solubilization of sludge and COD leakage

The soluble COD level of around 100 mg/L in the mixed sludge associated with the conceptual assessment mentioned above, although useful, becomes misleading without further evaluation, because it relates to *fresh sludge*. However, sludge never stays *fresh*. It contains significant fractions of active biomass and biodegradable particulate matter, and therefore, it undergoes a complex cycle of biochemical reactions involving decay, lysis, and hydrolysis leading to solubilization under anaerobic conditions (Bougrier et al., 2008; Camacho et al., 2003; Gardner et al., 2012; Harrison et al., 2006; Paul et al., 2006; Tomei et al., 2009). Uncontrolled anaerobic environment may occur during sludge holding within the settling tanks and thickeners. Furthermore, engineered anaerobic systems such as digesters are often selected as integral components of treatment plants for effective sludge stabilization and volume/mass reduction. This way, generated sludge generally spends between 2 and 24 h of process period actively contributing to substrate leakage, before dewatering and final disposal.

Evaluation of the complex sequence of biochemical reactions leading to substrate/COD solubilization, are usually simplified to an overall hydrolysis process, which may be defined in terms of an overall first-order reaction:

$$\frac{dX_T}{dt} = -k_h \cdot X_T \tag{12}$$

where X_T is the sludge concentration – expressed either in terms of volatile suspended solids (VSS) or cell COD – and k_h is the hydrolysis rate.

A number of studies applied this expression for evaluating the applicable hydrolysis rate, k_h for different components in the sludge; k_h was defined in the range of 0.05–1.94/d for carbohydrates, 0.0096–0.8/d for proteins, 0.005–0.7/d for lipids (Aldin, 2010; Carcia-Heras, 2003; Christ et al., 2000; Gujer and Zehnder, 1983; O'Rourke, 1986). Dimock and Morgenroth (2006), suggested a k_h range of 0.038–0.24/d for large protein particles and 0.09–0.98/d for small protein particles, yielding a mean k_h value of 0.3/d. The reported ranges are to be compared with the k_h value of 1.0/d calculated for the hydrolysis of settled sludge under aerobic conditions, basically indicating that hydrolysis proceeds much slower under anaerobic conditions (Okutman et al., 2001).

The effect of sludge hydrolysis on generated soluble COD and DOC may be visualized by continuing the mass balance exercise presented in Figs. 2 and 3, with the calculated mixed sludge concentration of around 14,000 mg SS/L, corresponding to 11,200 mg VSS/L and 15,700 mg cell COD/L. With the adoption of an overall k_h range of 0.1–0.5/d, the evolution of soluble COD and DOC generation with time spent in the treatment sequence before dewatering is plotted in Fig. 4, which shows that a soluble COD leakage of 260–1250 mg/L is likely to occur after 4.0 h and 1500–6000 mg/L after 24.0 h. The results also indicate that the DOC limitation of 80 mg/L will be exceeded between 2 and 12 h depending on the characteristics and rate of sludge hydrolysis (Fig. 4b).

4. Results and discussion

4.1. Observed soluble COD footprint

As previously mentioned, one of the two major components of the final DOC level measured after leaching is the initial level of dissolved organics included in the aqueous phase of the tested sludge. Estimation of the initial DOC level in the test requires evaluation of applicable sludge generation and stabilization processes within the treatment system. Related mass balance obviously depends on existing treatment steps (i.e., primary settling, aerobic stabilization, anaerobic digesters).

In this context, the monitoring program carried out for a period of around 6 months in 2013, during the survey of the selected wastewater treatment plant enabled to establish a footprint for the soluble COD, involving all the key steps in the sequence of both wastewater treatment and sludge handling. Fig. 5 illustrates the observed soluble COD footprint together with the corresponding DOC values. During the monitoring program, the plant received an average total COD, C_{T0} of 722 ± 110 mg/L; the soluble COD fraction, S_{T0} was 210 ± 13 mg/L, corresponding to a S_{T0}/C_{T0} ratio of 0.29, quite close to the level selected for conceptual appraisal. Parallel DOC measurements were not frequent enough to allow a statistical evaluation, but yielded a similar S_{T0}/DOC ratio of around 3.0; this ratio was used for calculating DOC levels throughout the plant.

As shown in Fig. 5, four different points were selected for assessing the footprint: Settled sludge streams from primary (PS) and final settling tanks (SS) (1 and 2); mixed sludge fed to the digester system (3) and the digester effluent (4). Major remarks related to the observed soluble COD footprint may be outlined as follows: (i) Significant soluble COD leakage started to occur during temporary sludge holding in the settling tanks: The soluble COD content of the primary sludge, S_{T1} was calculated as 820 ± 135 mg/L, exhibiting an almost 4-fold increase as compared to the influent soluble COD level of 210 mg/L; a similar increase was also observed for the secondary sludge from S_E of 50 mg/L in the plant effluent to S_{T2} of 200 mg/L in the sludge withdrawal stream. The results show that hydrolysis becomes an important process for the soluble COD balance and generation during settling, holding and withdrawal of settled sludge.

The impact of hydrolysis was much more visible through the thickening phase, which boosted the soluble COD level, S_{T3} to 2450 ± 460 mg/L in the mixed sludge before the digester feeding. At this stage, it should be noted that the plant includes two thickeners of different nature, the first one – a drum thickener – for the secondary sludge with no appreciable effect on soluble COD generation and the second – a gravity thickener with an average retention time of 24 h – serving the primary sludge and creating an uncontrolled anaerobic environment for auxiliary hydrolysis and COD solubilization. During the survey, the gravity thickener was observed to sustain an average VSS concentration of 33,600 mg/L. Calculations accounting for basic mass balance for sludge also indicated an average soluble COD level of 5400 mg/L due to hydrolysis of primary sludge during thickening, roughly corresponding to an overall hydrolysis rate k_h of 0.12–0.15/d, which remains within the bracket plotted in Fig. 4. This evaluation is also in agreement with results on limited fermentation of primary sludge, reporting a soluble COD generation of 4700 mg/L, mostly as volatile fatty acids, after 4.0 h of hydrolysis and acidification for an initial VSS concentration of around 23,000 mg/L (Cokgor et al., 2006). Later in a study investigating the effect of pH and temperature on primary sludge fermentation, a similar soluble COD and volatile fatty acid generation of 3800 mg/L and 3400 mg/L, respectively was obtained when the process was started with a slightly lower VSS concentration of 19,500 mg/L (Cokgor et al., 2009).

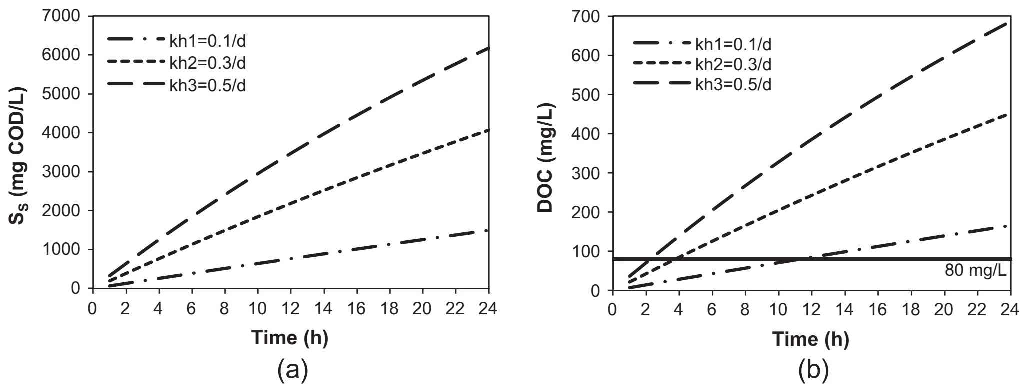

Fig. 4. Effect of hydrolysis period for the generation of (a) soluble COD; and (b) DOC.

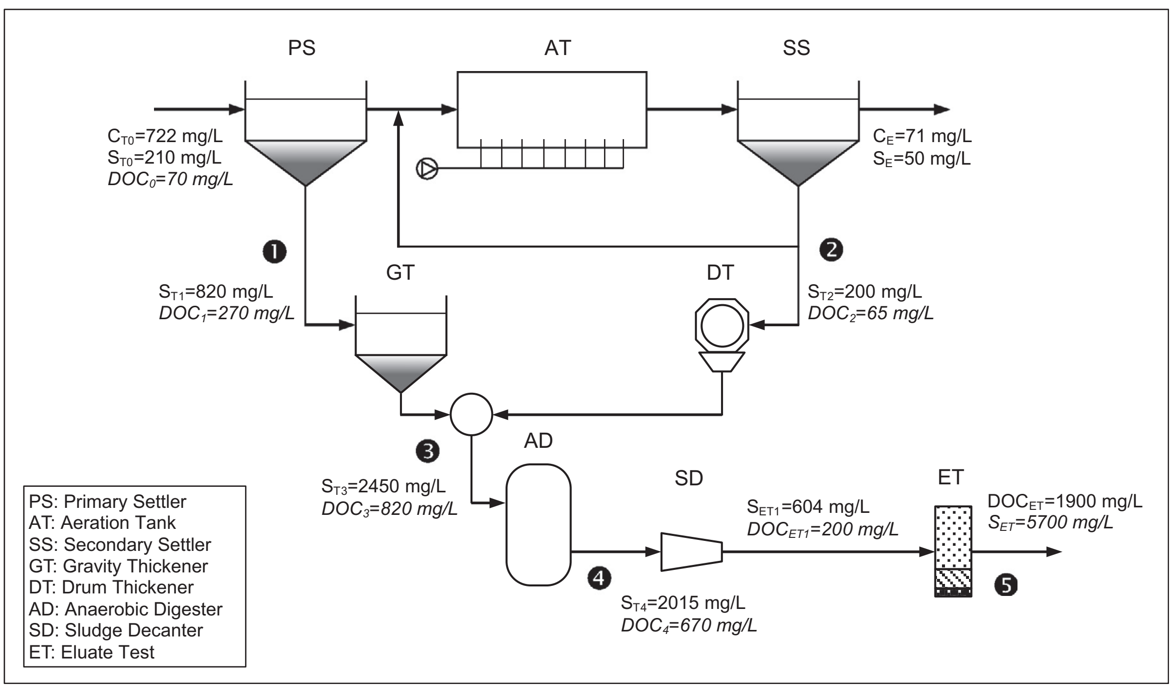

Fig. 5. Observed soluble COD footprint during the survey of treatment plant operation.

At the anaerobic digestion stage, which was observed to provide a VSS reduction of around 35–40%, the soluble COD level, S_{T4} was slightly reduced to 2015 mg/L, due to complex biochemical reactions associated with acetogenic and methanogenic activities of the microbial culture, leading to biogas/methane generation. The sludge processed in the digester mainly includes viable and non-viable complex organics, which first undergo hydrolysis, breaking them down to simpler soluable compounds, mostly volatile fatty acids. Therefore, the observed soluble COD level reflects the mass balance between its generation through hydrolysis and its utilization for microbial growth. Consequently, the reported difference between influent and effluent COD levels should not be interpreted at face value for interpreting the COD removal efficiency of the system, as it relates only to a fraction of complex biochemical conversions taking place during the ongoing anaerobic process. The centrifuged sludge dewatered to approximately 23% dry matter content, ended up with an average DOC level of 670 mg/L, prior to evaluation for final disposal.

4.2. DOC leaching during the test

In the eluate test – the last step of the footprint – soluble organic matter in the tested sludge is diluted as part of the experimental procedure to S_{ET1} of 604 mg/L and DOC_{ET1} of 200 mg/L, already substantially higher than the implemented upper limit, at the start of the experiment. This is quite significant, as it shows that the directive practically prohibits the landfilling application without having to perform the leaching test. In fact, the results of five different tests performed during the monitoring/evaluation period yielded an average DOC_{ET} of 1900 mg/L, corresponding to a soluble COD level, S_{TE} of 5700 mg/L as shown in Fig. 5, more than 20 times the prescribed limit.

It is interesting that in most of the leaching tests no effort is devoted to assess the initial soluble COD and DOC level before starting the experiment. This aspect was clarified in a specific leaching test performed on the same dewatered sludge, to visualize the fate of soluble COD. The test was started using a sludge sample

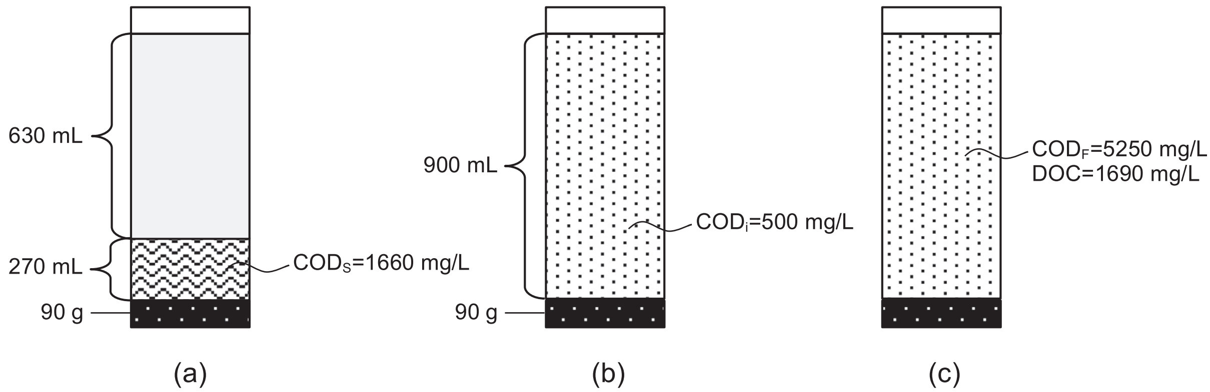

Fig. 6. Evolution of soluble COD and DOC in the eluate test (a) before dilution (b) after dilution (c) after one day agitation.

Table 2
DOC levels in the leakage tests of treatment plant with different configurations in Turkey (TUBİTAK KAMAG, 2013).

Type of wastewater treatment systems[a]	Number of WWTPs	DOC (mg/L)	
		Lowest	Highest
Conventional ASS	8	320	3950
Extended aeration	10	210	5370
Nutrient removal ASS	9	290	4550

[a] Flow rates: 2000–1,565,000 m^3/day.

(25% dry matter) with a soluble COD content (S_1) of 1660 mg/L. As indicated in Fig. 6, the procedure requires that the sample be diluted from 270 mL to 900 mL; this step reduces the initial COD in the test reactor (S_2) down to 500 mg/L (Fig. 6b). The procedure also dilutes the sludge concentration to 9% dry matter. After one day, the final soluble COD (S_3) was measured as 5250 mg/L, indicating a soluble COD leakage of 4750 mg/L during the test. The final DOC was measured as 1690 mg/L. This observation also enabled estimation of the overall hydrolysis rate to be expected for the tested sludge as 0.035/d, much lower than the rate associated with the hydrolysis reactions during thickening.

4.3. Observed DOCs in other treatment configurations

It may be argued that the treatment plant selected for the evaluation, although involving a typical configuration with anaerobic digestion, largely adopted in Europe, includes processes such as primary settling and/or gravity thickening that would not allow minimization of COD leakage from sludge. Results related to a large number of treatment plants with different flow schemes and functions are also presented here, mainly to clarify and satisfy a likely concern. In this context, the DOC results of the leakage tests derived from four different plants with internal (extended aeration) or external aerobic stabilization were reported in the range of 215–800 mg/L (Cokgor et al., 2012; Pehlivanoğlu-Mantas et al., 2007; Ozdemir et al., 2013). Similar results obtained from 27 different plants including, standard activated sludge, extended, aeration and different flow schemes for nutrient removal such as *A2O* and *Bardenpho* processes converge to an overall average DOC value of around 1000 mg/L as outlined in Table 2, regardless of process differentiation (TUBITAK KAMAG, 2013). The data presented in the Table 2 indicate that the reported DOC levels fluctuate between 210 and 5370 mg/L, depending on the type and characteristics of plant operation. Furthermore, Table 3 displays results of full analyses of two different leakage tests, as required by the directive; the first one with a DOC level of 313 mg/L relates to an extended aeration plant, and the second one with a DOC concentration of 1574 mg/L outlines the analytical data of one of the tests performed during the survey of the plant selected for this study. It is interesting to note that all measurements are in full compliance with corresponding limitations except for the DOC levels, which appear as the only regulatory obstacle for landfilling of the sludge.

5. Conclusions

The conceptual and experimental evaluation in this study provided conclusive proof for the fact that the DOC limitation of

Table 3
Analytical results of eluate tests from two different treatment plants.

Parameters	WWTP1 (This study)	WWTP2	Waste acceptance criteria for non-hazardous waste
Arsenic (As) (mg/L)	0.057	<0.025	0.05–0.2
Barium (Ba) (mg/L)	0.287	<1	2–10
Cadmium (Cd) (mg/L)	0.006	<0.002	0.004–0.1
Total chromium (Cr) (mg/L)	0.017	<0.025	0.05–1
Copper (Cu) (mg/L)	0.032	<0.1	0.2–5
Mercury (Hg) (mg/L)	<0.0005	0.746	0.001–0.02
Molybdenum (Mo) (mg/L)	0.009	0.075	0.05–1
Nickel (Ni) (mg/L)	0.004	<0.020	0.04–1
Lead (Pb) (mg/L)	0.006	<0.025	0.05–1
Antimony (Sb) (mg/L)	0.001	0.011	0.006–0.07
Selenium (Se) (mg/L)	0.004	<0.005	0.01–0.05
Zinc (Zn) (mg/L)	0.093	<0.2	0.4–5
Chloride (mg/L)	40	345	80–1500
Fluoride (mg/L)	<0.2	<0.1	1–15
Sulfate (mg/L)	8.94	926	600–2000
Dissolved organic carbon (DOC) (mg/L)	1574	313	50–80
Phenol index (mg/L)	0.32	0.15	–
Total dissolved solids (TDS) (mg/L)	2170	2020	400–6000

800 mg/kg DM (80 mg/L) imposed on treatment sludge is not attainable, and therefore not justifiable, on the basis of currently available technologies. Theoretical appraisal indicated no scientifically justifiable basis for this limitation and extensive experimental data collected for this purpose confirmed this appraisal, indicating that none of the leakage tests performed or envisaged in the study could come even close, let alone satisfy, the prescribed limitation. All observed results reflected 10 to 20-fold higher DOC levels than the numerical limit of 80 mg/L.

Therefore, this evaluation strongly suggested that the standard established by the directive should not be evaluated as "...*fair, equitable or based on scientific knowledge, for it may have been established arbitrarily on the basis of inadequate technical data*" (McGauhey, 1968). It leads to presume that it was defined *implicitly* to prohibit landfilling, without having to rely on a scientific *criterion* that should be based upon *best economically achievable technology*.

It is also quite difficult, *if not impossible*, to see the environmental benefit of this limitation, mainly because no effort was made to collect and evaluate any likely environmental impact of the COD leakage. It is recommended that future research efforts be directed to generate reliable scientific information on the nature and biodegradation characteristics of soluble COD formation.

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