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Advanced Oxidation with Nanofilm Photacatalyst'S on Stainless Steel Wire as Secondary Treatment of Wastewater

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Abstract: In this paper, authors reported the results of wastewater treatment of discharges from sanitary facilities and laboratories from de Metropolitan Autonomous University Azcapotzalco campus in Mexico city in a pilot plant integrated with a unit of coagulation-flocculation and sedimentation of suspended particulate and multilayer filtration with sand, zeolite and anthracite that filtered particulate higher than 5 nanometer of diameter as primary treatment and advanced oxidation based in the use of hydroxyl radical through ozonation and UV Photocatalysis with zinc oxide, zinc oxide doped with silver and zinc oxide doped with zirconia as fine films photocatalysts on a US 100 stainless steel wire as secondary treatment, and finally with activated carbon adsorption as final polish. COD and ORP were evaluated after each step as representative of BOD stablished as MAC's in Mexican regulation on wastewater effluents, obtaining values that comply with the regulation.

Key words: Advanced oxidation, nanofilms photocatalyst, secondary wastewater treatment.

1. Introduction

In Mexico, the wastewater treatment in general is carried on with biological oxidation of organic matter as secondary treatment. Treatment that has been effective to urban wastewaters. However, over the past decade instrument sensitivity has led to a wide detection of ng/L levels of emerging pollutants or organic micropollutants that include pharmaceuticals, personal care products, steroids, hormones, industrial chemicals and pesticides [1, 2]. Pollutants that are refractory to conventional biological treatment.

In this paper, authorsreported the results of the treatment with nano film photocatalyst as secondary treatment of waste water from the Metropolitan Autonomous University, Azcapotzalco campus in Mexico city, waste water that additionally of discharges from sanitary facilities have chemicals from laboratories and workshops that uses inks and pigments, that are released in continuous and batch discharges during the operating hours of the day, from Monday to Friday.

These discharges require new approaches in wastewater treatments. Photochemical processes are alternative to water treatments since UV irradiation in combination with other processes (e.g., ozonation, peroxidation or both) can remove bacterial substances from solution as well as dissolved organics. These photochemical oxidation reactions are now referred to as Advanced Oxidation Processes based in the ºOH oxidant (AOPs) [3] and recently the UV heterogeneous photocatalysis is included in this technique [4].

Advanced oxidation present advantages on conventional chemical oxidation because the process generates the oxidants in situ, there is no use of chemicals consumables as supplies, and as different from biological oxidation advanced oxidation could

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be a batch process and is not necessary to maintain a microbial population when there are toxics or exists abrupt changes in the temperature or pH in the raw water and the generation of residues are less than biological oxidation.

Additionally, biological oxidation use specialized microorganisms with the enzymes required to metabolize the substrate to generates energy and new biomass that require to be disposed in a safe manner. Microorganisms are present in consortiums and the ability of the microbial community to mineralized the organic matter is a function of their metabolic versatility [5].

Table 1 shows the general features of biological oxidation.

Biological reactors work 24 hours and must keep appropriate conditions in order that oxidize organic matter in terms of temperature, pH, available nutrients and oxygen as electron acceptor as well the substrate amount to support the oxidation process.

Microbial activity involves many reactions, according with the metabolism of carbohydrates that comprise the organic matter with lipids and proteins, the process involves at least four steps: glycolysis with 9 reactions to transform glucose C6 to Two pyruvates C3; pyruvates that when the supplied of oxygen is adequate is oxidatively decarboxylated to acetyl CoA which enters to citric acid cycle, where in 6 reactions, it is oxidized to carbon dioxide and water and trough electron transport in the respiratory chain that involves the transfer of electron to the oxygen as final acceptor in 6 reactions [7].

Transfer of electrons are involved in all the oxidation-reductions reactions, oxidation must be accompanied by simultaneous reduction, and the energy required for the removal of electrons in oxidation is supplied by the reduction, electron transport explain how oxygen enter the metabolism [7].

Energy transfer in the system is measured by difference in potential. In the biological oxidation, oxygen has the highest oxidation system in the living cell, and the process is catalyzed by enzymes which functions in combination with coenzymes or electron carriers [7].

Table 1 Biological oxidation requirements.

	Microorganisms	
Energy source	Energy Source	
Humidity	pH	
Nutrients	Temperature	
Not Toxicity	disposal of metabolites and excess of biomass	not competitive microorganisms
BIOLOGICAL OXIDATION		

Source: Adapted from Cookson [6] and Sutherson [7].

According with the previous concepts, biological oxidation involves many steps and additionally uses the oxygen as final electron acceptor which has an oxide reduction potential or ability to accept electrons (1.23 V) lower than oxidants used in advanced chemical oxidation such as hydroxyl radical (2.8 V), anion superoxide O^- (2.42 V), and ozone (2.07 V) [8]. In contrast, chemical oxidation involves less reactions and is faster than biological.

ºOH is an extremely reactive radical it reacts as soon as it is formed, additionally the hydroxyl radicals react non selectively with different compounds in the water. The amount of hydroxyl radicals formed is the limiting factor in these reactions, and there is a competition between compounds for the hydroxyl radicals [9].

Wastewater discharges from the UAM Azcapotzalco campus have an elevated organic content from sanitary and food facilities, as well as chemicals, solvents, acids and bases from laboratories of chemical environmental, and metallurgical engineering disciplines and additionally discharges from workshops such as pigments, inks and paints, substances that are refractories to biological oxidation.

Additionally, the discharges of raw material to feed the microbial population occurred from 6:00 to 21:00 hours in the day from Monday to Friday, without discharges Saturday and Sunday and holydays, that means that in these periods, there are not organic matter as substrates to support biological oxidation.

At the present, the campus has a wastewater treatment plant with a treatment train that receives triturated effluents, that are conducted to a coagulation-flocculation-sedimentation train, post filtered with anthracite, oxidized in a contact tank of ozone and finally filtered with activated carbon, before discharged to city sewer.

This study proposed to increase the treatment train with advanced oxidation with photocatalysis trough a nanofilm of zinc oxide over a stainless steel wire to obtain zero discharge using the treated wastewater to irrigates the campus gardens.

The proposed systems have the next features after triturate the raw water as pre-treatment as shown in Fig. 1.

1.1 Advanced Oxidation Principles

The conventional chemical oxidation use as oxidants consumable chemicals such as: chlorine, chlorine dioxide, sodium hypochlorite or potassium permanganate, substances that need storage with risks associated as well as expensive consumption.

Advanced oxidation implies the in situ formation of the hydroxyl ion ^{o}OH by photocatalysis, as well as others oxidants by secondary reactions, such as superoxide anion O_2^-, and hydrogen peroxide, oxidants that have an oxide- reduction potential, ORP higher than conventional oxidants as show in Table 2.

Hydroxyl radical could be formed from ozone in presence of water according the next reactions:

$$O_3 + H_2O \rightarrow O_2 + 2(\bullet OH) \quad (1)$$

$$O_3 + H_2O \rightarrow HO^- + 2(\bullet OH) \quad (2)$$

And by photocatalysis using a semiconductor, SC such as titanium oxide TiO_2 or Zinc Oxide ZnO, that exposed to UVC radiation lesser than 300 nm, liberate a free electron e^- that leaves a hole with a positive charge, since was in equilibrium, as shows in Fig. 2.

$$UV + MO \rightarrow MO\ (h + e^-) \quad (3)$$

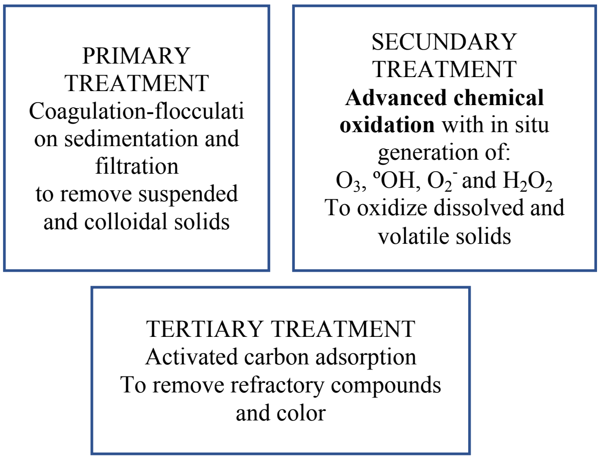

Fig. 1 Proposed system.

Table 2 Oxide-Reduction Potential—ORP of advanced and conventional oxidants.

Oxidant	E, Volts
$\bullet OH$	2.8
O_2^-	2.42
O_3	2.07
H_2O_2	1.78
ClO_2	1.57
Cl_2	1.36
O_2	1.23

Source: Siegrest, et al. [2].

The free electron moves from the valence orbital exposed to the UV radiation to a conduction orbital and translate to a final electron acceptor such as dissolved oxygen in water to avoid the reversible.

The free electron and the positive hole generated, reacts in presence of water as:

$$hv + (SC) \rightarrow e^- + h^+ \quad (4)$$

$$h^+ + H_2O \rightarrow \bullet OH + H^+ \quad (5)$$

$$e^- + O2 \rightarrow \bullet O_2^- \quad (6)$$

$$\bullet O_2^- + H^+ \rightarrow HO_2\bullet \quad (7)$$

$$HO_2\bullet + H^+ + e^- \rightarrow H_2O_2 \quad (8)$$

$\bullet OH$, $\bullet O_2^-$ and H_2O_2 can oxidize organic compounds (RH) or organic matter according the next reactions:

$$RH + \bullet OH \rightarrow \bullet R + H_2O,\ y \quad (9)$$

$$^{o}R + \bullet OH \rightarrow ROH \rightarrow CO_2 + H_2O$$

The photocatalytic effect has:

(a) Oxidative reactions:

$$h^+ + H_2O \rightarrow H^+ + \bullet OH \quad (11)$$

$$2\ h^+ + 2\ H_2O \rightarrow 2\ H^+ + H_2O_2 \quad (12)$$

$$H_2O_2 \rightarrow 2\ \bullet OH, \text{ and}$$

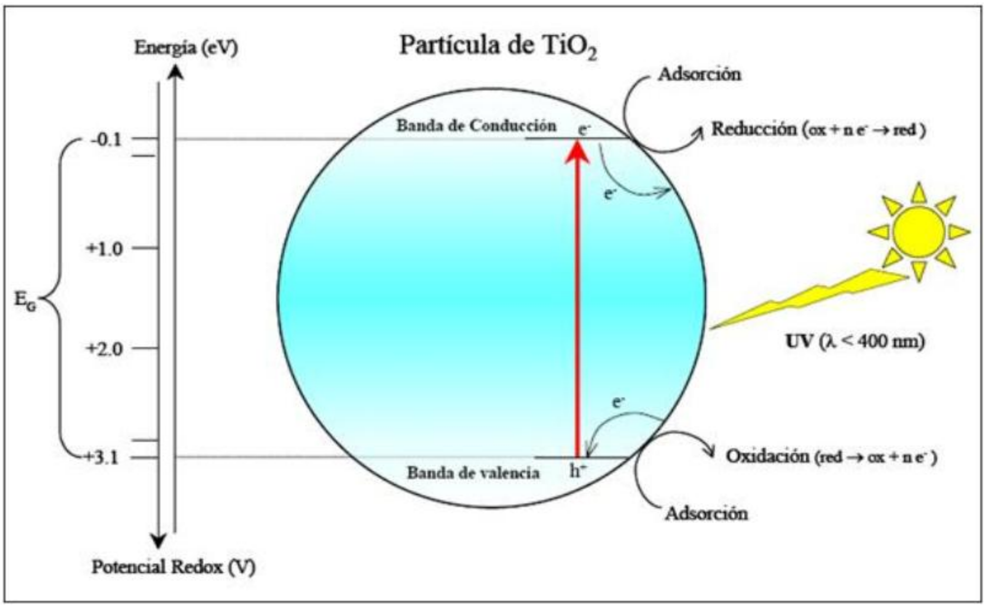

Fig. 2 Photocatalytic process [10].

(b) Reductive reactions:

$$e^- + O_2 \rightarrow \bullet O_2^-$$

$$\bullet O_2 - + HO\bullet_2 + H^+ \rightarrow H_2O_2 + O_2$$

$$HOOH \rightarrow HO\bullet$$

•OH has properties to attack virtually all the organic compounds including refractories to biological treatment, and compounds of low concentration (ppb), and reacts 10^6-10^{12}, faster than ozone, and generally the mineralization is complete, as different of conventional treatment, with a minimum amount of sludge's and improve the organoleptic properties of treated water [11].

In this project, instead of titanium oxide, authors use nanofilms of zinc oxide on a stainless steel US 100 wire, with a 149 microns open area, as well as zinc oxide doped with traces of silver and zirconium.

The purpose of zirconium doping was to increase the mechanical resistance and the silver doping to reduce the bandgap and increase the •OH formation.

2. Material and Methods

To develop the experiments, authors worked with the next Methodology:

(1) Manufacturing zinc oxide photocatalysis, with hydrolysis of zinc acetate as precursor in an electrodeposition cell, where the hydrolyzed precursor is deposited as zinc hydroxide (Zn_2OH) on the US 100 stainless steel wire, previously cleaned with isopropyl alcohol in an ultrasonic bath, and then calcined two hours at 500 ºC to obtain a ceramic film nanostructured of Zinc oxide (ZnO) as shown in Fig. 3.

(2) Manufacturing the zinc oxide photocatalyst doped with silver and zirconia. Adding traces of zirconium and silver sulfate in the electrodeposition process.

(3) Construction of treatment train (Fig. 3).

(4) Design experiment, using COD and ORP as independent variables after the ozonation and photocatalyst oxidation, and also color as dependent variable of pH.

(5) Characterization of raw water sample, measuring; COD, ORP, suspended solids (SS), Dissolved oxygen (DO), color and turbidity.

(6) Running the experiment by triplicate.

(7) Characterization the same parameters in each experiment phase.

(8) Analysis of data and discussion.

(9) Calculus of results and conclusions.

The Fig. 3, it shows the US 100 Stainless steel wire with and without the semiconductor thin film, this material can support the aqueous environment without corrosion, and with a low pressure drop to facilitate its use in the wastewater treatment.

The Figs. 4 to 9, it shows different sizes of the thin film electrodeposited on the wire with ZnO ceramic semiconductor and ZnO doped, presenting a big surface area, where the oxidation takes place.

Fig. 10 shows the composition of the material electrodeposited on the US 100 stainless steel wire, where Zn appears as well as the elements that are present in the steel.

Fig. 3 SS US 100 wire with/without a thin film of ZnO photocatalyst.

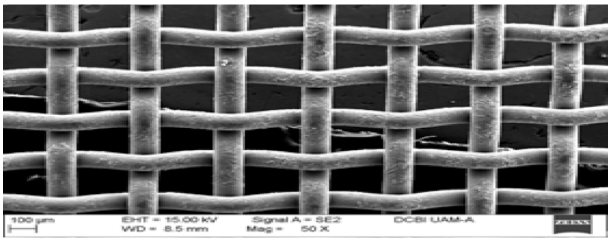

Fig. 4 MEB 50 X image of US 100 wire covered with a thin film of ZnO.

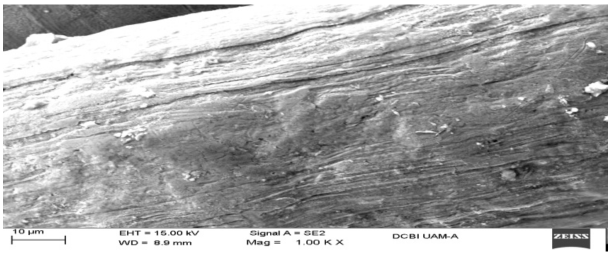

Fig. 5 MEB 1.0 KX image of US 100 wire covered with a thin film of ZnO.

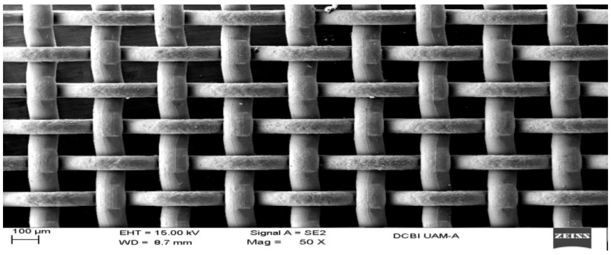

Fig. 6 MEB 50 X image of US 100 wire covered with a thin film of ZnO doped with zirconium.

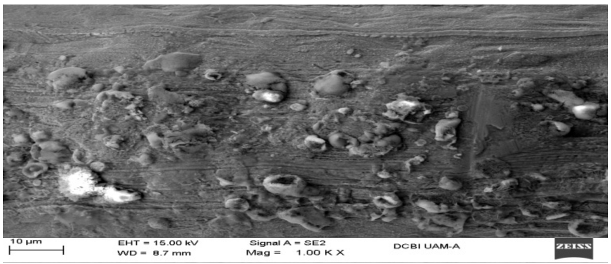

Fig. 7 MEB 1.0 KX image of US 100 wire covered with a thin film ZnO doped with zirconium.

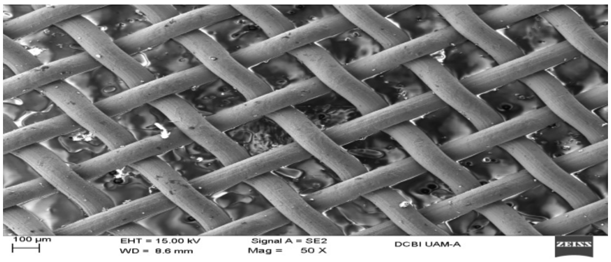

Fig. 8 MEB 50 X image of US 100 wire covered with a thin film of ZnO doped with silver.

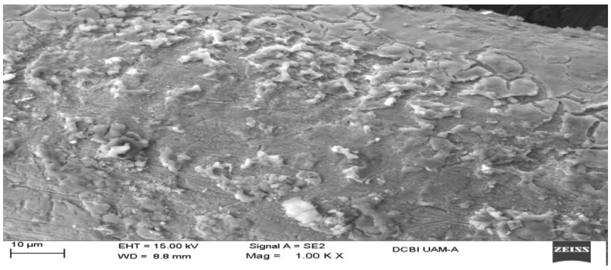

Fig. 9 MEB 1.0 KX image of US 100 wire covered with a thin film ZnO doped with silver.

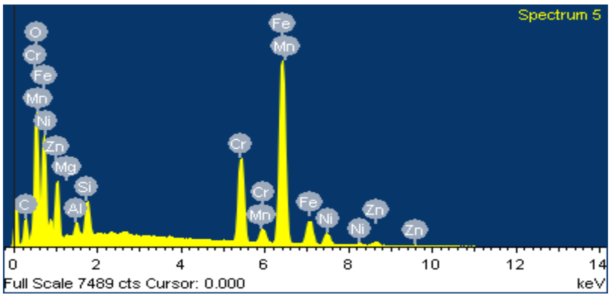

Fig. 10 Thin film ZnO on SS US 100 wire dispersive Energy spectrum.

The difractogramm in Fig. 11, shows the ZnO present in the wire, and the ZnO particulate, is a sample of the material electrodeposited on the surface of the US 100 SS.

The experiment was conducted in the treatment train of Fig. 12, where supplied air in up flow, to promote mixing, increase time of contact, and increment the dissolved oxygen.

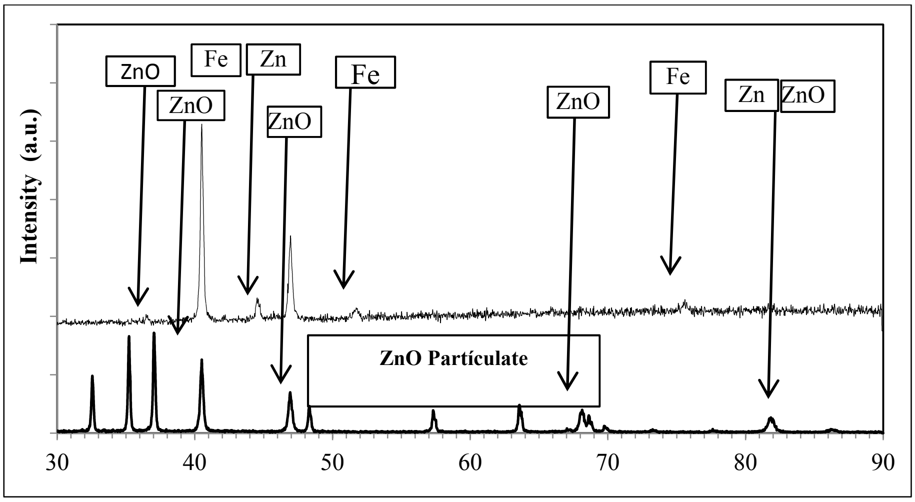

Fig. 11 US 100 SS wire covered with thin film of ZnO difractogramm.

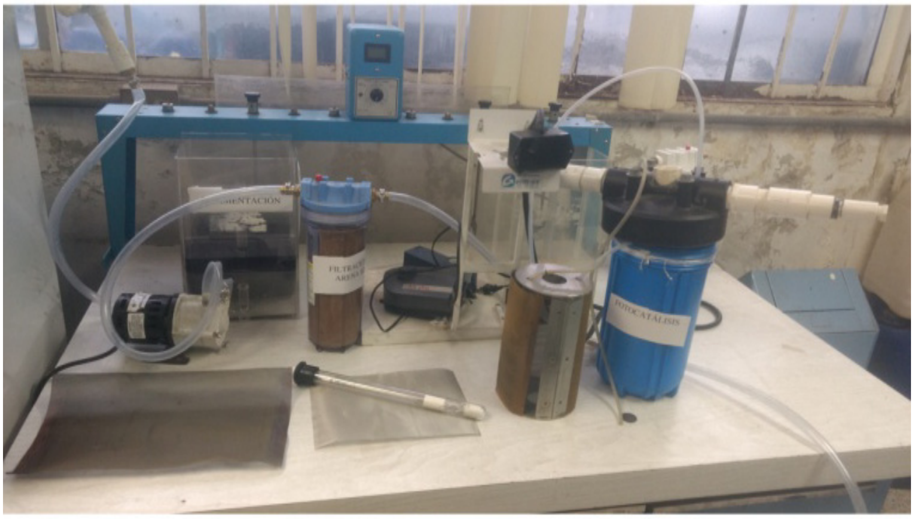

Fig. 12 Treatment train.

Table 3 Parameters trough the different treatment phases.

Sample	pH	SS mg/L	Color NTU	ORP Volt	DO m/L	COD mg/L
Raw water	7.46	384.3	1,400	-60	5.6	1,241.2
Multilayer Filtration	7.59	98.3	533.3	-43	6.3	513.7
Coagulation flocculation sedimentation	6.99	6.33	120.7	-60.7		437.9
Ozonation	7.98	9.0	183.3	-20.5	9.6	240.8
ZnO PC	8.92	9.0	210.33	16.7	9.8	186.3
ZnO PC Zirconium doped	8.71	6.7	154.7	-12.9	10.	195.5
ZnO PC Silver doped	8.55	6.3	155.3	-11.7	10.2	188.2
Activated carbon after ZnO PC	9.62	6.3	74	33.3	11.6	27.8
Activated carbon after ZnO PC zirconium doped	9.9	6.7	78.33	19.27	11.9	51.8
Activated carbon after ZnO PC silver doped	9.9	4.3	81.67	11.1	11.86	31.2

PC = Photocatalyst.

Table 3, shows the results in each phase of the treatment train.

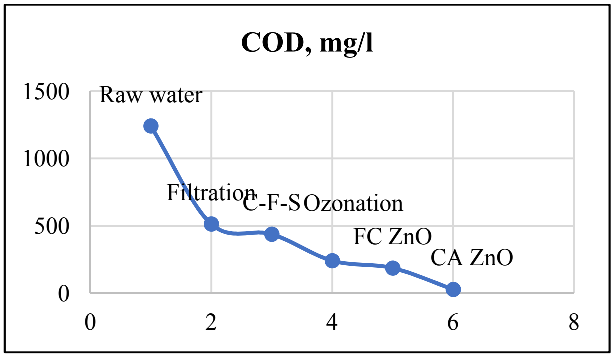

Fig. 13 COD in the treatment phases with ZnO photocatalyst.

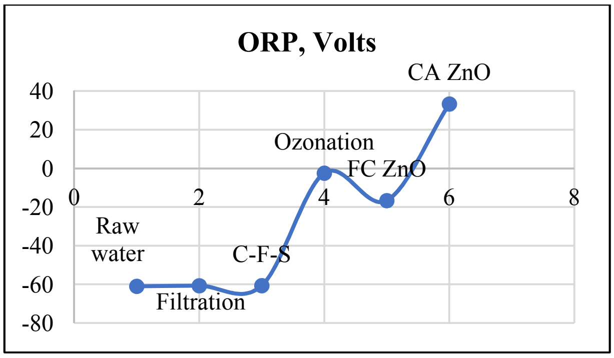

Fig. 14 ORP in the treatment phases with ZnO photocatalyst.

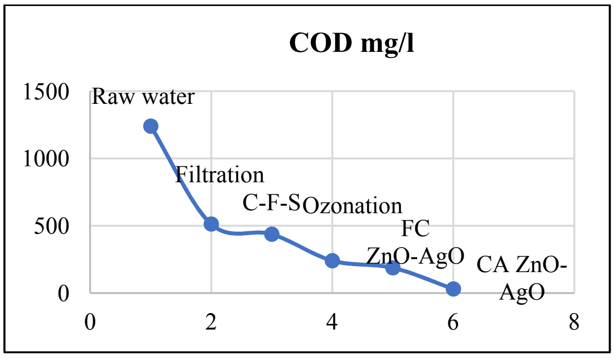

Fig. 15 COD in the treatment phases with ZnO-Ag photocatalyst.

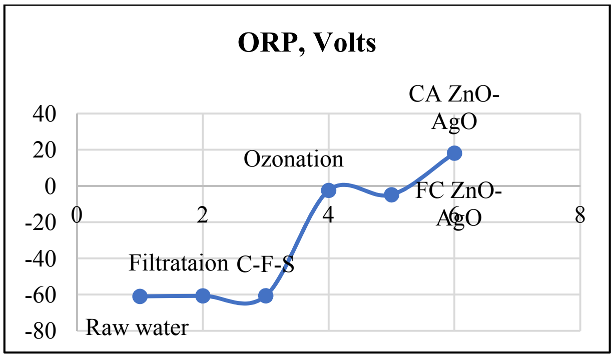

Fig. 16 ORP in the treatment phases with ZnO-Ag photocatalyst.

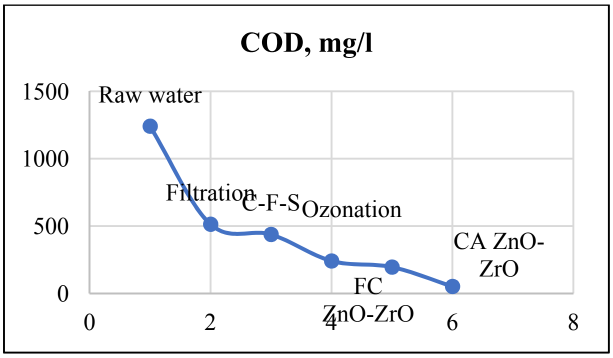

Fig. 17 COD in the treatment phases with ZnO-ZrO photocatalyst .

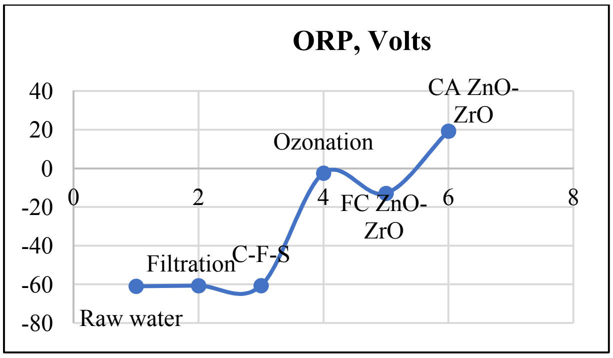

Fig. 18 ORP in the treatment phases with ZnO-ZrO photocatalyst.

3. Results and Discussion

These data show the next behavior in the treatment.

COD and ORP are considered as representative of inorganic and organic matter and the differences in each phase of the treatment could be representative of efficiency.

COD is related with BOD, which must be less that 60 mg/L according with waste water discharges on municipal services by Mexican rules, usually COD is higher than BOD.

ORP parameter is an indicator of the oxidation state of the water and it could be measured with an electrode or a direct reading instrument and evaluate the process in fast way, differences in the ORP values means that the oxidation happened.

As seen in the figures from 13 to 18, shows that the COD values were reduced to levels that can comply with the Mexican rule, maximum level allowed concentration, stablished by the Mexican rules, according with the oxidation registered with the ORP values that were incremented from the raw values to the oxidized water since.

4. Conclusions

Water treatment using these treatment trains, resulted successful, however, the advanced oxidation by itself is not enough to reach values that meet the rule 002, it is required the use of activated charcoal to make this happen.

According to the results shown, the best photo catalyzer was the Zinc Oxide, even though in the three cases, values that meet the rule were reached.

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The Survival and Vegetative Growths of a 60 Month-Old Tropical Rainforest Tree Species Trial Established under a *Hopea odorata* Nurse Stand at an Ex-Tin Mine in Peninsular Malaysia

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Abstract: AFoCo (Asian Forest Cooperation) Project in 2011 has funded a research and development project in Malaysia for enriching a mono-species stand established in an ex-tin mine. The project covered only for a period of 12 months. A study plot of 1 ha size was established in TTAC (Tin Tailings Afforestation Centre). Twenty indigenous tropical rainforest tree species were planted and their five year-old survival count, diameter and H (top height) growths are reported in this study. Some of them are red list species of IUCN (International Union of Conservation of Nature). The survival of the 1 ha planting trial was 53%. Mortality of the tree species is mainly caused by wild boars. The tropical rainforest tree species in this planting trial had similar growth to those planted at good mineral soils. This paper also documented the tending treatments which were implemented during post-planting that have contributed to healthy growth of the mixed-species stand. The mixed-species stand is being properly tended till to-date and hence sustained growth of the stand is anticipated.

Key words: Rainforest species trial, ex-tin mine, restoration, red-list tree species.

1. Introduction

Conversion of natural forests to various land uses for developing countries is a necessary evil along the social-economic pathway leading into a developed nation. Tin mining plays an important role for the economic development of Malaysia in the past three decades. Tin mining activities completely destroy the terrestrial ecosystem and reduce once diversified tropical rainforest into denuded ex-tin mines. To-date the extent of idle ex-tin mines was estimated to be about 80,000 ha distributed mainly in Perak and Selangor [1]. Ex-tin mine is an impoverished site comprising slime and sand tailings and has adverse microclimate for plant growths [2]. In addition, ex-tin mine has heavy metal pollutants such as arsenic and cadmium which are toxicants to plant growths [3]. Natural regeneration of ex-tin mines which are isolated from the natural forest comprising mainly only pioneer species normally was found in the early successional phase of open idle land or grassland, as there is lacking of seed sources from rainforest tree species [4]. FRIM (Forest Research Institute Malaysia) has developed the rehabilitation technologies for the greening ex-tin mines [5]. An ex-tin mine covering 121.5 ha was successfully greened by FRIM in 2002 and it is known as TTAC (Tin Tailings Afforestation Centre), which is located at Bidor, Perak in Peninsular Malaysia [6]. The greened site has been a model for rehabilitation of ex-tin mines in Malaysia and the

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region comprising 20 timber tree species [7]. AKECOP (ASEAN Korea Environmental Cooperation Project) supported the rehabilitation program in TTAC since 2002 and the project completed in 2016. Authors observed poor regeneration under man-made forest stands established on sand and slime tailings comprising species such as *Acacia mangium*, *Acacia auriculifomis*, *Hopea odorata* and *Khaya ivorensis* [8]. These man-made forests established in TTAC are but an island surrounded by farmlands, housing estates and oil palm plantation. The only small fragmented logged-over lowland forest nearby is Chikus Forest Reserve, which is located 15 km away from TTAC. Hence, only some woody tree and shrub species in the logged-over lowland forest that are dispersed by avian dispersal agents were found under the man-made forest stands. The species composition of the natural regeneration is lack of main climax tree species of lowland rainforest, as their seed dispersal agents are not birds or bats but big mammals, and/or, by winds [9]. Hence, further planting of selected climax rainforest tree species which are not found in the man-made forests was carried out in TTAC in 2011. This is part of the planting activity to fulfil one of the objectives stated in the blue print of TTAC; which is turning it eventually into a plant depository of tropical rainforest [10]. From 2013 till 2016, AKECOP funded the tending of the demonstration plot established by ASEAN-Korean Forest Cooperation Project (AFoCo) in the period of 2011-2012. The demonstration plot is a mixed stand of twenty rainforest tree species established under the nurse species *Hopea odorata*. This paper aims to document the survival and vegetative growth of the mixed stand of rainforest tree species established on a greened slime tailings site at five years after planting.

2. Material and Methods

2.1 Study Site

A study plot was divided into two subplots established under a ten-year-old *Hopea odorata* stand grown at slime tailings located in TTAC, Bidor, Perak, Peninsular Malaysia. The soil composition of the slime tailings in TTAC at 0-60 cm depth had 1.7-33.3% gravel (particle size > 2 mm), 31-38.7% sand (particle size between 0.05-2 mm), and 11.3-27.3% silt and clay (particle size < 0.05 mm). The study site has an average monthly rainfall of 283-290 mm, average daily maximum temperature of 34 to 35 °C, average mean daily minimum temperature of 22 to 24 °C, mean daily maximum irradiance of 1,600-2,500 $\mu mol \cdot m^{-2} \cdot s^{-1}$ [11]. The study plot was enriched with 20 indigenous tree species under-planting the ten year-old nurse stand of *H. odorata* with mean stand height and mean stand diameter of 13.3 ± 2.5 m and 6.7 ± 2.8 cm, respectively. The undergrowth mainly comprised of early pioneer plant species and they were cleared between the 4 × 5 m interspace of the two planting rows. The distance between two planting rows is 5 m apart. The slime tailings were then loosened to a depth of 1 m using a back-hoe machine. Planting hole of each planting point was dug manually with a specification of 30 cm radius and 50 cm depth. The planting distance was at 2 × 2 m for each planting point. The 1 ha plot is located between two forest roads namely Jalan Biodiversiti and Jalan Pasir in TTAC, it is further divided into two subplots of each 0.5 ha size. Subplot A is located adjacent to Jalan Biodiversiti and it was treated with burnt-rice husk and Subplot B which is located adjacent to Jalan Pasir acted as a control or without the treatment (Fig. 1).

For subplot treated with burnt-rice husk, the planting hole was then applied with ashes of burnt-rice husk of 1 kg per planting point mixed with the slime and refilled back to 20 cm. Another 1 kg burnt-rice husk was applied to each planting point at six months after planting. Burnt-rice husk treatment was found to be an insignificant effect on the survival and growth of the rainforest tree species grown under the nurse stand [12].

2.2 Planting Stock

The planting stock of the twenty selected indigenous

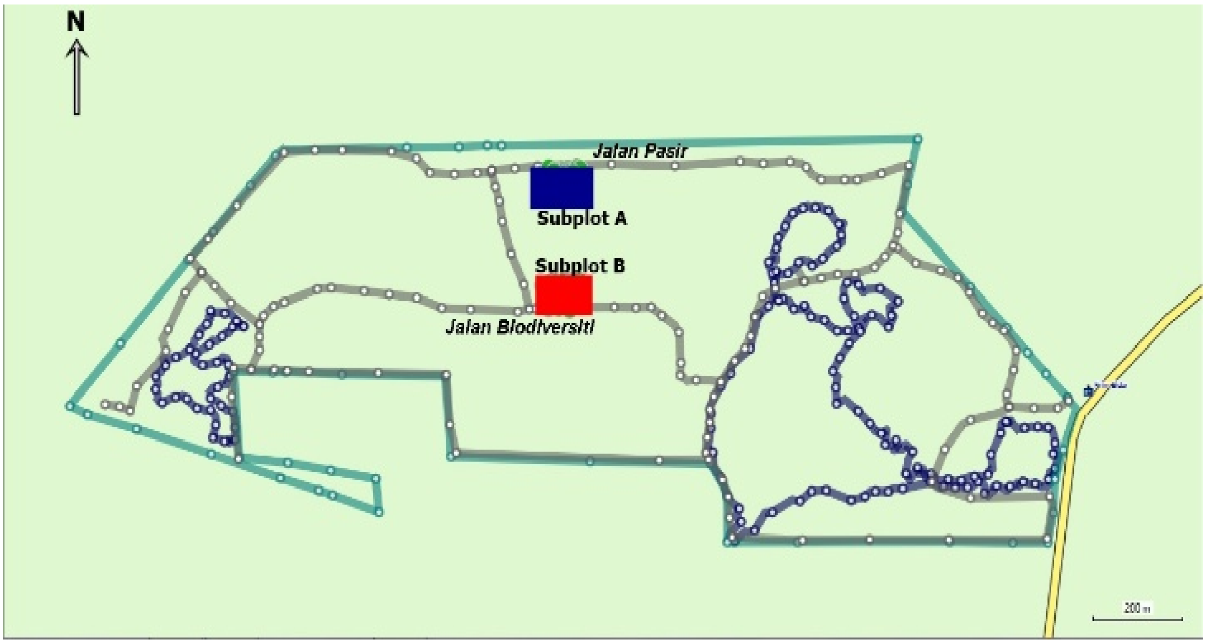

Fig. 1 **The location of the two subplots (not to scale) in TTAC.**

Table 1 **Tree species list for the planting trial.**

Non-dipterocarps	Dipterocarps
Garcinia hombroniana (NE)	**Shorea assamica* (CR)
Melaleuca cajuputi (NE)	*Shorea parvifolia* (NE)
Sindora coriacea (NE)	**Shorea acuminata* (CR)
Careya arborea (NE)	*Shorea curtisii* (LC/LR)
Cananga odorata (NE)	*Dryobalanops aromatica* (NE)
**Agathis borneensis* (EN)	**Hopea ferruginea* (CR)
Palaquium gutta (NE)	**Neobalanocarpus heimii* (VU)
**Aquilaria malaccensis* (VU)	**Shorea roxburghii* (EN)
Pentaspadon motleyi (DD)	**Shorea platyclados* (EN)
	Shorea ovalis (NE)
	Shorea macroptera (NE)

* denotes species listed in IUCN Red List Categories and Criteria Version 2.3 as threatened taxa include EN (Endangered), CR (Critically Endangered) and VU (Vulnerable). The other species are classified as NT (Near Threatened), LC (Least Concern)/LR (Lower Risk), DD (Data Deficient) and NE (Not Evaluated) [13, 14].

rainforest species were acclimatized in the TTAC for a period of three months prior to planting and they were distributed randomly in the two subplots. They have an average height of 45-50 cm and collar diameter of < 1 cm. They were planted during the wet season in December 2011. These species planted in the enrichment program are listed in Table 1. Eight of the twenty rainforest tree species is referred to as threatened species according to IUCN (International Union of Conservation of Nature) Red List version 2.3 (Table 1), of which two are non-dipterocarps and six dipterocarps.

2.3 Tending Regime

Tending practices including weeding together with loosening of soils and fertilizer application were carried out at two-month and three-month intervals, respectively. Weeding includes blanket weeding using environmentally safe weedicide sprayed at 50 cm away from each planting point, then followed by circle weeding manually within the 50 cm radius of the planting point. Loosening of soils within 50 cm radius was carried out together with the circle weeding. The planting point was further enriched with additional nutrients from the application of a mixture of organic fertilizer comprising 80% chicken manure with 10 g NPK (15:15:15) at three-month intervals. Watering was carried out during the first year after planting during the dry periods of April, June and July 2012, with an average monthly rainfall of 80 ±10 mm. The mean daily evapotranspiration is at 4 mm·day^{-1} [5]. No more watering after the second year but weeding and loosening of soils were carried out till to-date.

2.4 Survival and Growth Parameters

Each species was planted with 36 seedlings in each subplot. Hence, total seedlings of 20 rainforest tree species are 720 seedlings per subplot. The survival of each species was computed accordingly as number of survived seedlings × 100%/36. Each planting point of the surviving species was ground positioned using a ground positioning satellite receptor, Garmin Rino 650. The diameter at breast height (dbh) was measured at 1.4 m above ground level using a Richter fiber-glass diameter measuring tape with diameter graduation readable to mm. The top height (H) of saplings and trees was measured using a telescopic height measuring stick (Fig. 2). Mean diameter or height annual increment is calculated by mean diameter or height divided by five years (Mean dbh/5 or H/5). Initial height range of the seedlings for all the species was from 30 to 50 cm.

3 Results and Discussion

3.1 Survival

Survival counts were carried out in June 2012, May 2013, July 2015 and June 2017. The survival of the enrichment species is reduced from an average of 91.8% to 53% from 2012 to 2017, respectively (Table 2). The distribution of each species in Subplots A & B is recorded in GPS map (Fig. 3). Mortality of the planting is mainly due to destruction of seedlings by wild boars which contributed to 80% of the total mortality of the mixed stand (Fig. 4), the other remaining 3% was due to root diseases and 17% due to adaptability of the species. Wild boars uprooted the seedlings in the first two years, and later debark them and eventually they were killed during the drought seasons. Similar problem is also recorded for a planting of indigenous timber species in logged-over forest in Peninsular Malaysia, 60% of the mortality was due to wild boars [15].

Generally, dipterocarp species had higher survival count than non-dipterocarps grown on the greened slime tailings (Table 3). *Shorea roxburghii* had survival more than 80%, this species is known to be suitable for adapting in open conditions especially in open planting but lower than the planting on good mineral soils under *Acacia mangium* as a nurse stand [15, 16], followed by *Neobalanocarpus heimii* and *Dryobalanops aromatica*. *Shorea platyclados* in this study had the lowest survival of 54.2%, as it severely suffered from wild boar attacks. However, despite

Fig. 2 Height measurement of the rainforest trees grown under the *Hopea odorata* stand.

Table 2 Survival (%) of tropical rainforest species grown on greened slime tailings.

	Quantity	7/11/11	12/6/12	13/5/13	14/7/14	15/7/15	17/6/16
Subplot A	720	100%	98.3%	75.1%	62.2%	54%	50%
Subplot B	720	100%	91.8%	76.1%	64.7%	59%	56%
Mean		100%	95.1%	75.6%	63.5%	56.5%	53%

* Seedlings were planted in Nov. 2011 & refilling was done in May 2012.

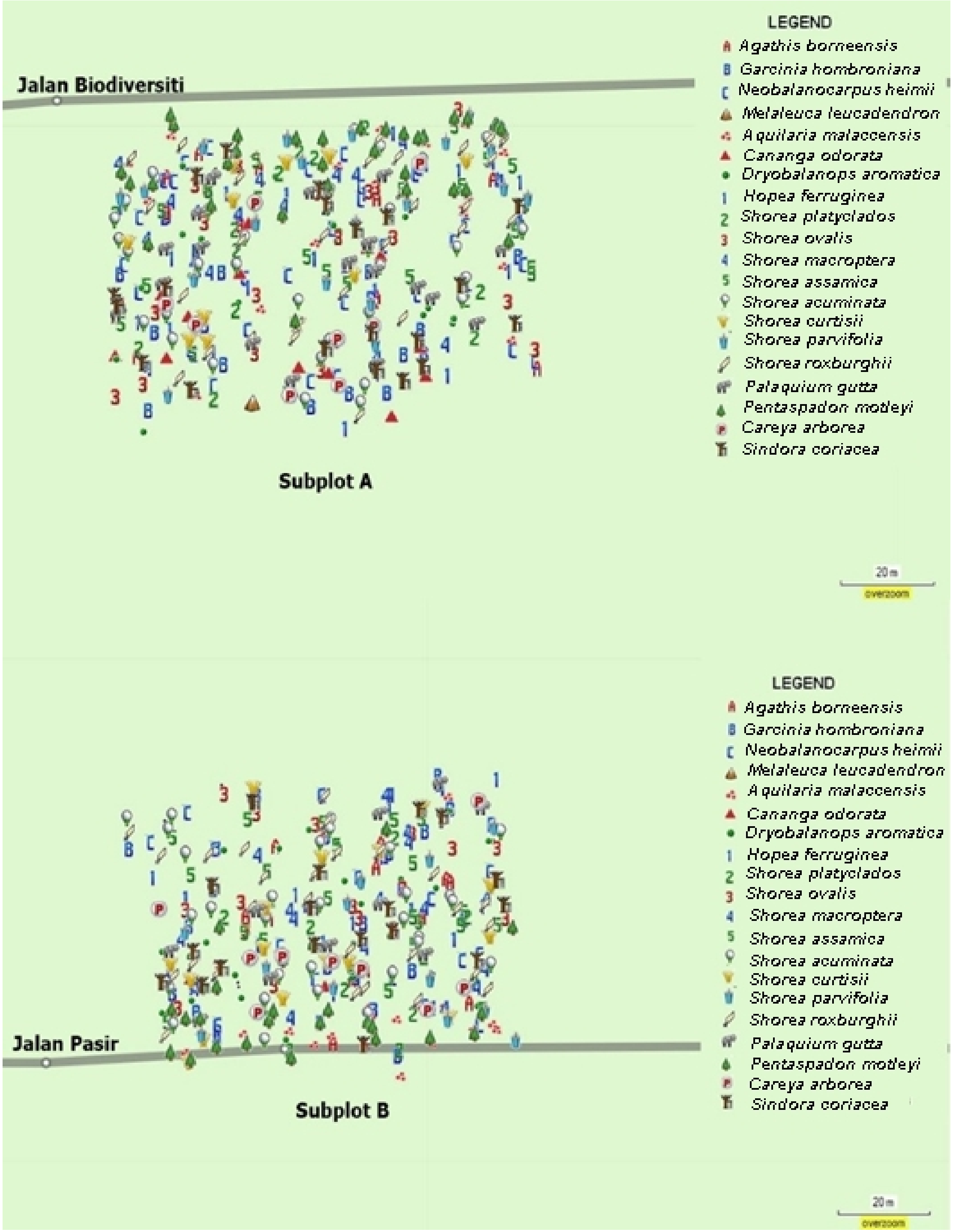

Fig. 3 Distribution of the surviving species in Subplot A at Jalan Biodiveristi and Subplot B at Jalan Pasir.

Fig. 4 Debarking of trees by the wild boars which eventually killed the five year-old *Dryobalanops aromatica*.

Table 3 Survival of rainforest species grown on the greened slime tailings at five years after planting.

No.	Species	Survival (%)		
		Subplot A	Subplot B	Mean
	Dipterocarps			
1	*Shorea roxburghii*	86.1	86.1	86.1
2	*Neobalanocarpus heimii*	80.5	63.9	72.2
3	*Dryobalanops aromatica*	75	66.7	70.8
4	*Shorea parvifolia*	72.2	55.6	63.9
5	*Shorea acuminate*	63.9	63.9	63.9
6	*Shorea curtisii*	55.6	55.6	55.6
7	*Shorea macroptera*	55.6	55.6	55.6
8	*Shorea assamica*	47.2	63.9	55.6
9	*Shorea ovalis*	52.7	55.6	54.2
10	*Hopea ferruginea*	55.6	47	51.3
11	*Shorea platyclados*	33.3	50	41.6
	Non-dipterocarps			
12	*Pentaspadon motleyi*	80.5	80.6	80.6
13	*Sindora coriacea*	50	50	50
14	*Agathis borneensis*	41.7	50	45.8
15	*Aquilaria malaccensis*	36.1	55.6	45.8
16	*Garcinia hombroniana*	52.8	25	38.9
17	*Palaquium gutta*	47.2	27.8	37.5
18	*Cananga odorata*	11.1	11.1	11.1
19	*Careya arborea*	13.8	8.3	11
20	*Melaleuca cajuputi*	0	2.7	1.35

growing in an impoverished slime tailings site, it has the same range of survival as it was planted in a good mineral soils of a logged-over forest. A study showing that *Shorea platyclados*, *S. parvifolia* and *S. assamica* were line planted in a logged-over forest at Tapah Forest Reserve had survival of 48.2%, 67% and 89.9%, respectively at 60 months after planting [15]. Similarly, *Neobalanocarpus heimii* grown in slime tailings had better survival than those planting under the nurse stand of *Acacia mangium* established on good mineral soils which had only 9 to 13% survival at 76 months after planting [15].

For survival of the selected non-dipterocarps planted under the *Hopea odorata* stand, *Pentaspadon motleyi* had the highest survival followed by *Sindora coriacea*, and the lowest survival group of species comprising of *Cananga odorata, Careya arborea* and *Melaleuca cajuputi.* No survival was recorded for *Melaleuca cajuputi* in Subplot A, one of the reasons other than being destroyed by wild boars through uprooting it during the seedling phase, is due to its low adaptability in growing under shade. *Melaleuca cajuputi* is a strong light demander grown gregariously and dominantly in open and acidic conditions of coastal swales-sand dunes in Malaysia [17]. Lower survival of *Cananga odorata* under shade is anticipated as it is also a strong light demander and grows as plantation crop in open condition for essential oil production and is highly sought in the fragrance industry. *Careya arborea* is also another species more susceptible to the wild boar attack thus has lower survival.

3.2 Mean dbh and MAID (Mean dbh Annual Increment)

The mean dbh and MAID are tabulated in Table 4. Based on the growth assessment, twenty species of rainforest tree species could be grouped into four groups. The first group comprises of *Shorea acuminata, S. parvifolia*, and *S. platylados* are relatively fast growers and have their range of dbh from 6.2 to 6.9 cm (Table 4). The second group of rainforest species had mean range of dbh from 4.8 to 5.1 cm including *Shorea ovalis*, *S. macroptera, S. curtisii*, *Hopea ferruginea* and *Pentaspadon motleyi*. The third group of tree species namely *Shorea assamica, Neobalanocarpus heimii*, *S. roxburghii*, *Cananga odorata*, *Palaquium gutta*, *Agathis borneensis*, *Sindora coriacea* and *Garcinia homobroniana* had a mean dbh range from 3.6 to 4.8 cm. Lastly, *Careya arborea* was identified as the slowest grower due to its low drought tolerant morphological properties and also easily attracts wild boar attacks. Their MAID follows the same trend of mean diameter growth (Table 4).

Shorea parvifolia in this study has similar MAID with other finding when it was grown in a good mineral soil through similar type of planting method. Periodic mean diameter annual increment of *S.*

Table 4 Mean dbh and periodic MAID of the tree species at five years after planting.

	Species	Subplot A	Subplot B	Mean dbh (cm)	MAID (cm/y)
1	*Shorea acuminata*	7.9 (2.5)	5.9 (1.4)	6.9 (1.9)a	1.38 (0.39)
2	*Shorea parvifolia*	7.2 (2.4)	6.4 (3.2)	6.8 (2.8)a	1.36 (0.56)
3	*Shorea platyclados*	6.7 (2.4)	5.8 (2.5)	6.2 (2.4)a	1.25 (0.49)
4	*Dryobalanops aromatica*	5.1 (2.1)	5 (1.7)	5.0 (1.8)b	1.01 (0.37)
5	*Shorea assamica*	5.7 (2)	4.4 (1.1)	5.0 (1.6)b	1.01 (0.31)
6	*Shorea ovalis*	5.4 (1.4)	4.5 (2.2)	5.0 (1.8)b	0.99 (0.36)
7	*Shorea macroptera*	4.9 (1.8)	4.8 (1.5)	4.8 (1.6)b	0.97 (0.33)
8	*Shorea roxburghii*	3.8 (2.1)	4.5 (1.7)	4.2 (1.9)c	0.83 (0.38)
9	*Shorea curtisii*	4.8 (2)	3.5 (1.2)	4.2 (1.6)c	0.83 (0.32)
10	*Cananga odorata*	3.5 (1.1)	4.7 (1.9)	4.1 (1.5)c	0.82 (0.3)
11	*Hopea ferruginea*	4.4 (1.4)	3.5 (0.9)	4.0 (1.2)c	0.79 (0.23)
12	*Palaquium gutta*	2.2 (1.1)	4.4 (1.2)	3.3 (1.15)cd	0.66 (0.23)
13	*Garcinia hombroniana*	3.1 (1.1)	3.2 (1.1)	3.2 (1.1)cd	0.63 (0.22)
14	*Neobalanocarpus heimii*	2.8 (1.1)	3 (1.2)	2.9 (2)d	0.58 (0.23)
15	*Agathis borneensis*	2.7 (1.1)	3 (0.8)	2.8 (0.95)cd	0.57 (0.19)
16	*Aquilaria malaccensis*	2.2 (1.1)	2.8 (1.1)	2.5 (1.1)d	0.5 (0.22)
17	*Pentaspadon motleyi*	2.2 (0.8)	2.8 (1)	2.5 (0.9)d	0.5 (0.18)
18	*Careya arborea*	1.6 (0.57)	1.6 (0.7)	1.6 (0.63)de	0.32 (0.12)
19	*Sindora coriacea*	2.9 (1.2)	2.97 (1.3)	1.2 (1.2)e	0.24 (0.25)
20	*Melaleuca cajuputi*	-	3.4	-	0.68

() denotes standard deviation and different alphabetical letters denote significant differences by *t*-test at 0.05 level.

Table 5 Mean H and MAIH (Mean Top Height Annual Increment) of the tree species.

No.	Species	Subplot A	Subplot B	Mean H (m)	MAIH (m/y)
1	*Shorea parvifolia*	8.7 (3.2)	7.5 (2.5)	8.1 (2.8)a	1.6 (0.6)
2	*Shorea platyclados*	7.9 (2.3)	6.6 (2.2)	7.2 (2.2)a	1.45 (0.45)
3	*Aquilaria malaccensis*	7.2 (1.9)	6.9 (1.8)	7.0 (1.8)a	1.41 (0.37)
4	*Dryobalanops aromatica*	7.4 (1.9)	7.1 (2.1)	7.2 (2)a	1.4 (0.4)
5	*Shorea acuminata*	7.9 (2.5)	5.9 (1.4)	6.9 (1.9)ab	1.38 (0.45)
6	*Shorea ovalis*	7 (1.6)	5.8 (1.9)	6.4 (1.8)b	1.28 (0.35)
7	*Shorea macroptera*	6.4 (1.9)	6.2 (2.2)	6.3 (2.0)b	1.26 (0.41)
8	*Shorea curtisii*	6.8 (2.6)	5.4 (1.7)	6.1 (2.2)b	1.22 (0.43)
9	*Pentaspadon motleyi*	4.4 (2.3)	7.2 (2.8)	5.8 (2.6)bc	1.16 (0.51)
10	*Hopea ferruginea*	6.5 (1.1)	5 (1.4)	5.8 (1.6)bc	1.15 (0.25)
11	*Cananga odorata*	4.1 (1.8)	5.6 (1.6)	4.8 (1.7)c	0.97 (0.34)
12	*Shorea assamica*	3.6 (1.9)	6 (1.4)	4.8 (1.6)c	0.96 (0.33)
13	*Shorea roxburghii*	3.8 (2.1)	5.7 (2.3)	4.8 (2.2)c	0.95 (0.44)
14	*Palaquium gutta*	4.3 (1.1)	4.4 (1.2)	4.4 (1.2)c	0.87 (0.23)
15	*Agathis borneensis*	3.4 (1.5)	4.4 (0.9)	3.9 (1.2)c	0.78 (0.24)
16	*Neobalanocarpus heimii*	3.7 (1.8)	3.8 (1.4)	3.8 (1.6)c	0.75 (0.32)
17	*Sindora coriacea*	3.6 (1.2)	3.9 (1.3)	3.8 (1.2)c	0.75 (0.25)
18	*Garcinia hombroniana*	3.5 (1)	3.8 (1.3)	3.6 (1.12)c	0.73 (0.23)
19	*Careya arborea*	1.9 (1.2)	1.4 (1.2)	1.6 (1.2)d	0.33 (0.24)
20	*Melaleuca cajuputi*	-	6.6	6.6	1.32

() denotes standard deviation and different alphabetical letters denote significant differences by *t*-test at 0.05 level.

assamica and *S. platyclados* planted under a logged-over forest is reported to be 1.0 and 0.6 cm•y^{-1}, respectively, at 60 months after planting [18]. Both the species in this study had greater MAID than those grown in a good mineral soils at a logged-over forest. Similarly, *Shorea macroptera* and *Neobalanocrpus heimii* had greater MAID than those planted in good mineral soils [15-17, 19].

3.3 Mean H and Mean Annual Top Height Increment

The mean H and periodic mean height annual increment of twenty species of rainforest tree species could be grouped into four groups. The first group comprises of *Aquilaria malacensis*, *Shorea parvifolia*, *S. platyclados*, *Dryobalanops aromatica* and *S. accuminata*, which are relatively fast growers and have their range of H from 6.9 to 8.1 m (Table 5). The second group of rainforest species had mean H of 5.8 to 6.4 m including *Shorea ovalis*, *S. macroptera*, *S. curtisii*, *Hopea ferruginea* and *Pentaspadon motleyi*. The third group of tree species namely *Shorea assamica*, *Neobalanocarpus heimii*, *S. roxburghii*, *Cananga odorata*, *Palaquium gutta*, *Agathis borneensis*, *Sindora coriacea* and *Garcinia hombroniana* had a range of H from 3.65 to 4.85 m. Lastly, *Careya arborea* was identified as the slowest grower due to its low drought tolerant morphological properties and also easily attracts wild boar attacks. A single remaining tree of *Melaleuca cajuputi* was excluded from the ranking.

Similarly, mean height annual increment follows the same trend as the mean H. Interesting to note that *Shorea platyclados*, *Neobalanocarpus heimii*, *S. parvifolia*, *S. curtissi*, *Agathis borneensis* and *Pentaspadon motleyi*, *S. accuminata*, *S. macroptera*, *Sindora coriacea* and *S. curtisii* are species used for enriching the timber stock in logged-over forests which have good mineral soils [15, 16, 18, 19]. They are now proven to survive and grow healthily in a greened slime tailings site under the nurse stand of *Hopea odorata*. The single tree of *Melaleuca cajuputi* left in the planting trial is growing at the edge of the plot which is at open condition hence it has high diameter and height growths.

4. Conclusion

Based on the results of survival and vegetative growth parameters of the mixed-species stand grown on slime tailings, most of selected tropical rainforest tree species are suitable for growing on the improved slime tailings through under-planting the nurse stand except strong light demander such as *Melaleuca cajuputi*. It is important to highlight the good growth for most of the species in the five year-old mixed stand is largely contributed by the proper tending practices being implemented. To reduce further mortality caused by wild boars to the mixed stand, a research on how to prevent the wild boar attacks may need to be conducted. The tending practices of the mixed-species stand developed in this study provide a plantation know-how to further enrich a successful rehabilitation phase of ex-tin mine from a mono-species stand to a mixed-species stand which will eventually lead to restoration success of turning barren ex-tin mine into a man-made tropical forest.

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Analysis of Sludge Settling and Rising Behavior in Sewage Treatment Plant in Kuwait

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Abstract: All wastewater treatment plants in Kuwait utilize the activated sludge processes in the removal of organic matter and nutrients from domestic sewage. The efficiency of solid liquid separation in the activated sludge system is determined by the ability of sludge constituents to remain flocculated and to settle fast. In Kuwait's wastewater treatment plants, solids separation problems may occur in activated sludge system, such as bulking sludge, which affects the quality of the secondary effluent. The main aim of this paper is to study and analyze sludge settling and rising behavior in the activated sludge process of Jahra sewage treatment plant. The results indicated that clarifier effluent has significant suspended solids carry-over, which is eventually removed in the sand filtration process. In addition, test results showed poor settlement of clarifier sludge. The poor sludge settling is related to insufficient oxygen level in the aerators. Suggestions were made to raise oxygen level particularly in the aeration unit.

Key words: Sludge, sewage, treatment, carry-over.

1. Introduction

Discharge of untreated wastewater directly to the environment, will cause pollution of the receiving waters and spread of waterborne diseases. In the early years of the twentieth century the method of biological treatment was invented, and nowadays forms the basis of wastewater treatment worldwide [1]. In Kuwait and because of severe environmental impact of dumping wastewater into sea, several wastewater treatment plants have been constructed and operated since 1968 [2]. In recent years, treatment of wastewater in Kuwait has become essential not only for environmental protection of aquatic ecosystem but also for augmenting limited water resources by reusing of treated wastewater [3]. The collected sewage in Kuwait is treated in four main wastewater treatment systems located at Um-Alhaiman, Sulaibiya, Riqqa and Jahra. The sewage treatment plants in Kuwait generally employ the activated sludge treatment process. In this process, the microorganisms metabolize and transform organic and inorganic substances into environmentally acceptable forms, and they proliferate and grow as flocs [4]. These flocs are allowed to settle to the bottom of the tank, leaving a relatively clear water free of organic material and suspended solids. Many problems can develop in conventional sewage plants especially in the activated sludge operation that adversely affect the final effluent quality [5]. Sludge bulking and rising are common and serious problems in activated sludge operation, which affect most activated sludge plants at one time or another. Sludge rising or bulking usually occurred in an activated sludge plants when the sludge does not settle easily and has an excessive volume. Poor sludge settling is due to the excessive proliferation of filamentous bacteria, foaming due to growth of certain microorganisms and poor flocculation properties of the microorganisms [4]. This can lead to carry over from the final effluent clarifies. A bulking sludge is usually characterised by a sedimentation rate of less

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than 0.3 m/h, or an SVI (Sludge Volume Index) of above 150 mL/g [6]. The aim of this study is to investigate sludge settling behavior in the aerator tank and common observations such as floating sludge in clarifier and high average SVI in Jahra wastewater treatment plant.

2. Jahra Sewage Treatment Plant

The Jahra sewage plant is located at the northwest of Kuwait city and adjacent to Jahra satellite town. It started operation in 1983 with an average design capacity of 86,000 m^3/d. Present inflow is 65,000 m^3/d. The plant consists of EASP (Extended-Aeration Sludge Process) with clarifier, and tertiary treatment. As it has no primary clarifiers, raw wastewater flows directly from the preliminary treatment (coarse screening and grit removal) level to EASP units and then to the tertiary treatment units. The sludge is wasted from the aeration basins and thickened in a sludge gravity thickener. The thickened sludge is wasted and is applied on drying beds for drying and subsequent disposal. A schematic diagram of unit processes of Jahra sewage plant is shown in Fig. 1.

Table 1 presents the technical data of the sludge treatment processes of Jahra wastewater treatment plant.

3. Materials and Methods

In this study, samples were collected once in each week from designated locations for 12 months starting from May 2004 and ending in April 2005. Samples were collected from three critical points representing the performances of the unit processes. The sample points as shown in Fig. 1:

- Aeration tank effluent line (sample point 1);
- Return sludge line (sample point 2);
- Thickener wastage sludge line (sample point 3).

All parameter determinations in the laboratory were performed according to the Standard Methods. Both chemical and biological analyses were carried out at the laboratories of the DRP (Doha Research Plant) and at Sulaybiya Wastewater Research Plant. The methods

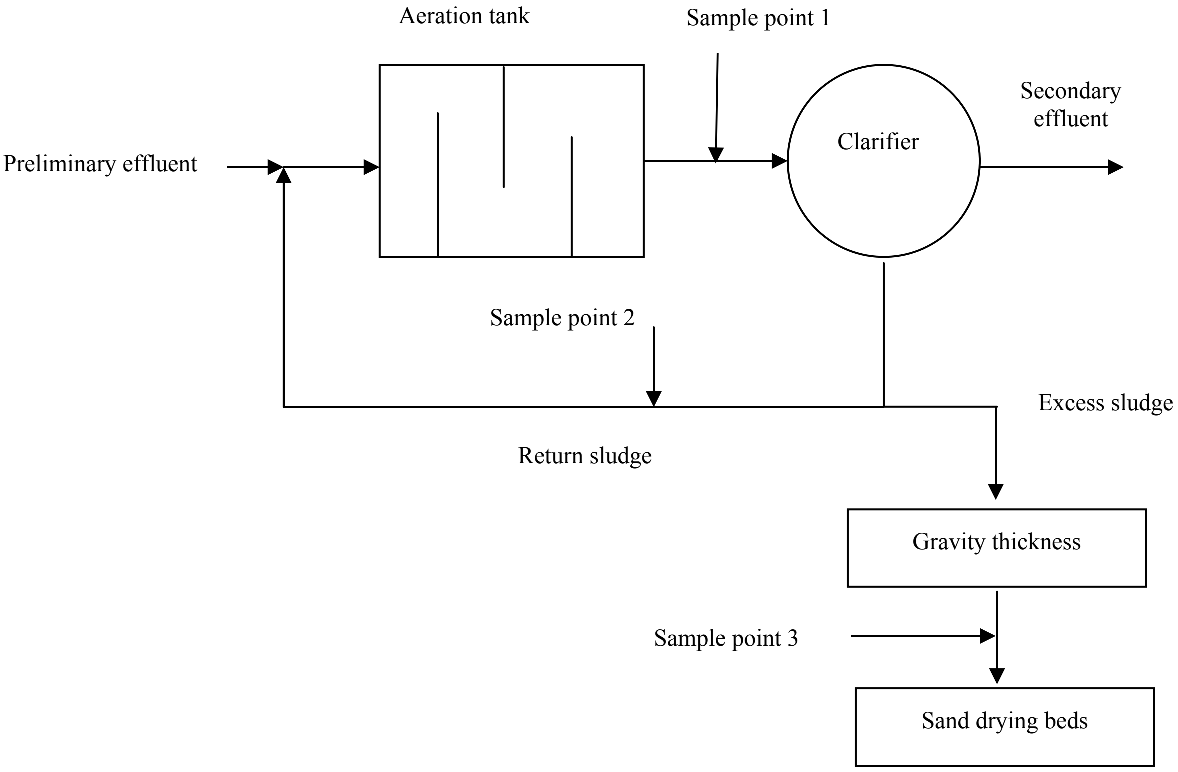

Fig. 1 Schematic diagram of extended aeration sludge process in Jahra sewage plant.

Table 1 Technical data of unit processes of Jahra sewage treatment plant.

Equipment	Unit	Description
Return sludge screw lift station		
Type		Open screw-Type
Number each	4	
Diameter	mm	1,600
Lift	m	5.6
Capacity	m^3/d	86,000
Motor	kW	50
Sludge thickeners		
Type		Circular, with full scraper and central
Number of units		2
Diameter	m	1.5
Sidewall depth	m	3.7
Surface area per unit	m^2	284
Volume per unit	m^3	727
Total surface area	m^2	567
Total volume	m^3	1,455
Sludge drying beds		
Type		Evaporation/percolation
Number of beds		3
Cells per bed		10
Cell Size:		
Length	m	25
Width	m	15
Surface area per cell	m^2	375
Total area, 4 beds	m^2	15,000

used in analyzing the chemical and biological parameters were according to the standard methods for the examination of water and wastewater [7]. In addition, sludge samples were collected for settling tests. In this test, one sludge sample from sludge recycle line was tested for determining the settling characteristics of sludge. The results are used to understand the sludge settling and rising behavior in activated sludge system, in addition, guide the operators to control the clarifier bottom-sludge recycle functions and compare the operating loadings with typical loading guidelines of similar clarifiers.

4. Results and Discussion

4.1 Activated-Sludge Settling in Clarifier

The clarifier performance with respect to solids separation through solids compaction is shown in Table 2. Important parameter is clarifier bottom TSS (Total Suspended Solids) which when compared with aerator effluent TSS, indicates sludge compaction factor in the clarifier. Average TSS in recycle sludge was recorded to be 6,114 mg/L when maximum and minimum values are 8,260 and 2,720 mg/L respectively. When the values are compared with those of clarifier-inflow (aerator-effluent) as presented in Table 3, the sludge compaction factor is about 1.5, which is very low when compared to expected value of 2-3 [8, 9].

Four main observations such as occasional high carry over of TSS with clarifier effluent, low average sludge TSS concentration of 6,114 mg/L in clarifier underflow (Table 2), floating sludge in clarifier (as shown in Figs. 2 and 3) and high average SVI (≥ 150 mL/g) indicated that the settling of sludge in the aerator has some problem. It is not performing at normal solid-liquid separation at desired levels of sludge-compaction. The loading rates in Jahra clarifier in sludge mass and hydraulic flow are about 1.9 $kg \cdot m^{-3}$ and 9.85 $m^3 \cdot m^{-2} \cdot d^{-1}$ at flow rate of 67,000 m^3/d and 4,660 g/m^3 (mg/L). Jahra plant is an extended aeration system. The expected ranges of mass and hydraulic loadings are 1-5 $kg/m^3/d$ and 8-16 $m^3/m^2/d$ respectively. Therefore, the loadings are normal and there should not be any reason for poor sludge settling.

Table 2 Statistical summary of Jahra recycled sludge quality (Data point 5).

Parameter	Average	Std. dev.	Max	Min
Temperature (°C)	28.4	4.4	34	21
BOD (Biochemical Oxygen Demand)				
TSS	6,114	1,147	8,260	2,720
VSS (Volatile Suspended Solids)	2,637	668	3,960	800
TDS (Total Dissolved Solids)	1,352	165	1,650	1,030
Total N	30.1	3.1	32.3	27.9
PO_4	13.3	8.6	28	1.9
pH (unit)	7.4	0.14	7.6	7.1
Chloride	268	65	380	130
Oil & grease	14	5	28	6
Alkalinity as $CaCO_3$	514	229	800	150
SO_4	400	118	650	190
Sulfide	0.3	0.39	1.2	0.03

All concentrations in mg/L or as indicated.

Table 3 Statistical summary of Jahra aerator effluent quality.

Parameter	Average	Std. dev.	Max	Min
TSS	3,917	779	5,560	1,960
VSS	1,616	371	2,415	590
TDS	1,392	235	2,500	1,020
Total N	23.9	5.7	30.4	16.5
Org. N	5.4	1.2	6.9	3.9
NH_3	13	2.4	15	9.6
Nitrite N	0.8	0.7	2.4	0.4
Nitrate N	5.1	3.3	12	2.1
PO_4	21	5.7	32	12.5
Alkalinity as $CaCO_3$	437	186	660	140
Temp. °C	30.1	2.78	35	22
pH (unit)	7.4	0.2	7.8	7
SO_4	421	120	630	200
Sulfide	0.6	0.5	2.4	0
Chloride	267	52	320	150
O_2	0.8	0.7	4	0.3
Oil & grease	18.4	9.3	56	7

All concentrations in mg/L or as indicated.

Other possible causes may be bulking sludge, rising sludge and trapped gas bubbles in sludge. These factors along with possible remediation should be studied further to device corrective measures. With a poor settling or bulking sludge, solids carryover in the effluent will contribute to higher effluent. Poor sludge compaction will result in a low concentration of return sludge solids, which in turn will limit the concentration of MLSS (Mixed Liquor Suspended Solids) that can be maintained in the aeration basin.

4.2 Settling of Inflow Suspended Solids

Aerator effluent data as shown in Table 3 indicated average TSS and VSS concentrations of 3,917 and 1,616 mg/L respectively. Volatile suspended solids are about 41% of total suspended solids. The fraction in typical activated sludge is between 60-75%. It indicates somehow in the system inorganic fraction is building up. One of the causes may be the absence primary sedimentation tank in the system. Removal of inflow settleable solids in primary sedimentation prior to aerator would assist to raise the TSS/VSS ratio.

4.3 Sludge Thickener

Table 4 contains the statistical summary of long-term weekly measurements of wastes sludge from sludge thickener unit. Average TSS concentration in thickener bottom-sludge is 17,576 mg/L when maximum and minimum values are 31,100 mg/L and 4,960 mg/L respectively. When compared with inflow TSS of 3,917 mg/L (average), the compaction factor is about 4.5. Average compaction is normal. Average, maximum and minimum values of total-N are 22.1, 23.5 and 20.6 mg/L respectively. The content of total N in sludge does not fluctuate significantly. Nitrogen and PO_4 levels indicate significant fertilizer value of the wasted sludge.

Table 4 Statistical summary of wastage sludge quality (Data point 6).

Constituent	Average	Std. dev.	Max	Min
Flow (m^3/d)	709	337	1,240	20
TSS	17,576	7,037	31,100	4,960
VSS	8,059	3,255	14,310	1,820
TDS	1,272	139	1,550	1,060
Total N	22.1	2.1	23.5	20.6
NH_3	9	4.2	12	6
PO_4	14.1	9.3	31	2.1
pH	7.3	0.1	7.7	7
Coliform, colony/100 mL	10×10^7	6×10^7	18×10^7	4×10^7
F. coliform, colony/100 mL	3.7×10^6	3.3×10^6	9×10^6	0.6×10^6

All concentrations in mg/L or as indicated.

4.4 Sludge Settling Test

SVI is usually measured of aerator effluent to test the settleability of sludge. It indicates the sludge settlement behavior in the clarifier. The test is performed for a 30-minute sludge settlement in a cylinder or cone and the result is expressed as gram-mass of settled sludge per milliliter volume of settled sludge. The index value ranging between 40 and 120 mL/g indicates excellent settleability. Eight SVI values determined at separate occasions had an average of 150 mL/g with maximum and maximum of 200 and 125 respectively. In addition, physical appearance of the Jahra clarifiers (Fig. 2) shows lots of floating sludge indicating rising sludge characteristics. These observations prompted the investigators to carry a sludge settlement test in laboratory for longer duration with variable concentrations of initial sludge-solid contents. Sludge settling test apparatus is shown in Fig. 3. Subsidence rate of sludge-blanket (interface of sludge and top clean-water) with time was measured at various times. Collected data along with calculated linear blanket subsidence-velocity and solids flux due to gravity are shown in Table 5.

SVI is defined as the volume in milliliters occupied by one gram of activated sludge after a one-liter mixed liquor sample has been allowed to settle in a graduated cylinder for a period of 30 minutes, or

$$SVI\ (\frac{ml}{g}) = \frac{setlled\ sludge\ volume,\ (\frac{ml}{l})}{suspended\ solid\ concentraion, mg/l} * \frac{1000mg}{g}$$

Fig. 2 Floating sludge in clarifier.

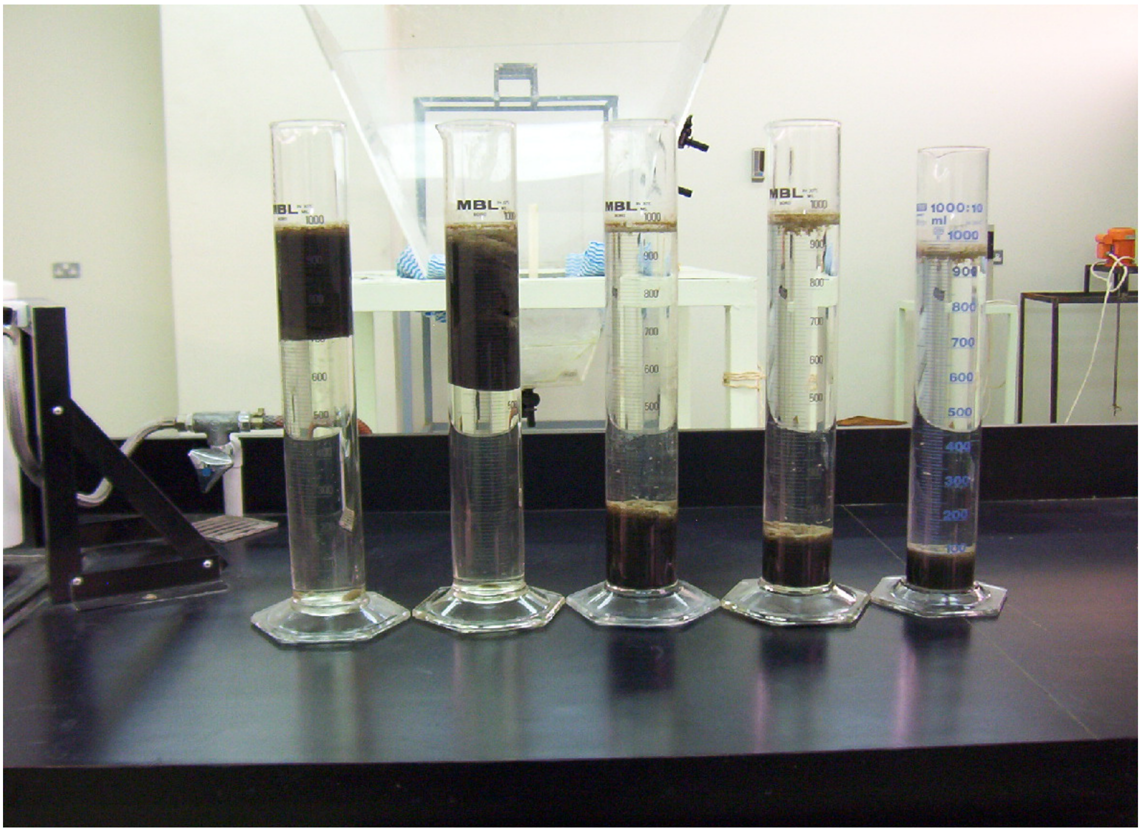

Fig. 3 Cylinder tests for secondary sludge settlement.

Table 5 Sludge balnket settlement with time and gravitational solids flux.

MLSS Concentration (g/m^3)	Time of Settlement (min)	Sludge blanket depth from water surface (cm)	Linear velocity of blanket settlement (m/h)	Solids gravity flux ($kg/m^2/h$)
15,345	60	14.5	0.14	2.15
10,200	60	24.3	0.24	2.45
5,830	20	24	0.72	4.2
4,660	15	31.5	1.3	6.06
3,490	5	26.3	3.15	11
1,400	5	30	3.6	5.26

SVI value is an important indicator of sludge settlement. SVI values were consistently found to be above 150 mL/g. The SVI values of good settling sludge range from 40 to 120 mL/g. [9]. Though it is not an absolute test for classifying poor settlement, however, its consistent higher values have significance. Sludge bulking and rising were noticed in the laboratory tests within 24 h of retention (Fig. 3). Two anticipated causes for floating sludge are Rising sludge and Bulking sludge.

4.5 Rising Sludge

Occasionally sludge that has even good settling characteristics will be observed to rise or float to the surface after a relatively short settling period. The causes of this phenomenon are denitrification. Nitrogen gas produced in the process makes the sludge mass buoyant causing sludge rise. In extended aeration process such as Jahra, a significant portion of nitrogen is converted to nitrate. Long period of detention of sludge in the clarifier is prone to generating such gas. From the observation of floating sludge in the clarifiers, gas entrapment remains to be a viable cause. Rising sludge problem can be overcome by:

1. Increasing sludge recycle rate from the bottom of the clarifier.
2. Decreasing the rate of inflow into the offending tank provided sludge depth could not be reduced by increasing recycle rate.
3. Decreasing the mean cell residence time (sludge retention time in the process) by increasing the sludge wastage rate.
4. Gentle stirring to release the trapped gas bubbles.

4.6 Bulking Sludge

A bulked sludge is one that has poor settling characteristics and poor compaction. From the measured suspended solids in the recycle line, Jahra plant has poor compaction with compaction factor much less than expected. In this respect, sludge can fall in bulking sludge group also. However, as mentioned earlier further study exploring all possible causes is necessary to confirm the major cause(s). Main causes of sludge bulking include fluctuations in flow and waste strength, pH, temperature, staleness, nutrient content and nature of wastewater components. The Jahra plant is operating at its average design conditions. Therefore, design limitations are not expected to be a major factor. Plant operation should be checked for maintaining proper oxygen level in aerator, recycle flow according to inflow conditions and overall cleanliness of channels and tanks to keep them free of grease accumulation, algae growth, scum accumulation etc. Nitrogen and phosphorus levels in the aerator tank appear to be normal (Table 3). However, if industrial waste is introduced intermittently, nitrogen and phosphorus levels should be carefully checked. They may favor certain type of bacterial growth such as algae making imbalance in bacterial population distribution in the process. Algae has poor settling behavior. The region's high ambient temperature and sunny conditions favor algae growth. Limited dissolved oxygen is more frequently noted than any other cause for sludge bulking. The data collected on oxygen level in the aerator are consistently around 0.5 mg/L. It is expected to be in between 1-2.5 mg/L. Therefore, it is recommended that under the conditions, to confirm whether the oxygen level is the cause, the blowers should be operated at full capacity to maintain at least 2 mg/L oxygen. Operating the system under this condition for a while and observing sludge settling characteristics simultaneously may confirm oxygen deficiency as one of the causes. If this level of oxygen cannot be maintained, the solution to the problem may require the installation of additional blowers.

5. Conclusion

Clarifier has the tendency of carrying over suspended solids occasionally, which may create increased maintenance problem of subsequent tertiary units such as sand filter. Secondary sludge was found to have poor settling characteristics creating problems of floating sludge in the clarifier and relatively low solids concentration in the clarifier bottom sludge. A primary sedimentation tank is essential to reduce the existing suspended solids in aerator.

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Certified Reference Material for Determination of Total Cyanide in Soil [BAM-U116/CGL306]

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Abstract: CRM (Certified Reference Material) BAM-U116/CGL306 "Cyanide in soil" was produced within a framework of cooperation between CGL (Central Geological Laboratory) of Mongolia and Federal Institute for Materials Research and Testing (BAM) of Germany in 2013-2017. The CRM BAM-U116/CGL306 represents a mixture of a sandy soil collected from a contaminated former gasworks area in the Berlin region (Germany) and an unpolluted sandy soil from Nalaikh region (Mongolia). The bulk candidate material for this reference material was prepared at CGL CRM Laboratory exclusively destined to the preparation of reference materials and equipped with modern technical equipment. Homogeneity, stability and shelf life were studied in full compliance with ISO Guide 35. The CRM was evaluated as sufficiently homogeneous. Statistical evaluation of certification analysis was software packages SoftCRM and ProLab Plus. Certified value of total cyanide of the CRM is 12.0 mg/kg and expanded uncertainty was assigned as 0.8 mg/kg. The intended purpose of this material is the verification of analytical results obtained for the mass fraction of total cyanide in soils and soil-like materials applying the standardized procedure ISO 11262:2011. As any reference material, it can also be used for routine performance checks (quality control charts) or validation studies.

Key words: CRM, cyanide in soil, total cyanide.

1. Introduction

Cyanide compounds in the environment originate mainly from a variety of industrial sources, such as the electroplating industry, blast furnaces, coke producing plants and gasworks. Due to their toxicity, cyanides are among the most important inorganic pollutants to be tested and monitored not only in the aquatic environment, but also in soils and soil-like materials. They can be determined as easily liber table cyanide, as complex cyanide or as total cyanide. However, in any case it should be kept in mind that the obtained measurement results are operationally-defined referring to the applied analytical method. To make such analyses comparable, strict adherence to an agreed analytical protocol is an essential prerequisite. The aim of the project described in this report was to certify a reference material on the basis of the International Standard ISO 11262 [1] which specifies a normative analytical method for the determination of total cyanide in soil. According to the prescribed analytical protocol cyanides are liberated from the test sample using ortho-phosphoric acid. The released hydrogen cyanide is transported by an air flow and absorbed into a sodium hydroxide solution. The absorbed cyanide is then quantitatively determined either by a photometric method or a titrimetric method using an indicator.

2. Candidate Material

The candidate CRM (Certified Reference Material) BAM-U116/CGL306 (Central Geological Laboratory306) was prepared as a mixture of a sandy soil collected from a contaminated former gasworks area in the

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Berlin region (Germany) and an unpolluted sandy soil from Nalaikh region (Mongolia). The two raw materials were processed separately at BAM and CGL, respectively. They were dried at ambient air to constant mass and then passed through a vibrating 2 mm sieve discarding the fraction > 2 mm. Afterwards, the material passing the sieve was grounded to particle sizes below 125 µm. Blending and homogenization of the two soil fractions < 125 µm as well as bottling of the final candidate CRM were performed at CGL. A total of 1,000 units with (100 ± 3) g of soil each were filled up into 100 mL plastic (HDPE) containers equipped with a screw cap with tamper evident ring. After bottling the whole batch was stored at (20 ± 3) °C.

3. Homogeneity Study

A total of 15 bottled units of the candidate material were selected using a stratified random sample picking scheme following the sequence of bottling to give complete coverage of the production batch. From each unit three independent test portions of 5.0 g were analyzed using CFA (Continuous-Flow Analysis) method according to ISO 17380 [2] (after extraction of cyanides from the soil sample with 2.5 mol/L sodium hydroxide solution). Compared to ISO 11262, this method may give slightly different results for the total cyanide content. However, as stated in ISO 17380 "these differences are not considered to be very significant", and therefore, there was no reason to question the suitability of the CFA method for homogeneity testing. Its main advantages are the high level of automation, the large sample throughput and adequate repeatability. From all selected bottled units each one sub-sample was analyzed together under repeatability conditions in one run with one calibration. To minimize the risk of a possible calibration bias between the different sub-sample runs, each time two additional control samples were analyzed. The results obtained for these control samples were used to normalize the calibration status of the subsequent measurement series. All measurement results from the homogeneity study are given in Appendix I. The estimate of inhomogeneity contribution u_{bb} to be included into the total uncertainty budget was calculated according to ISO Guide 35 [3] on the basis of the results of 1-way analysis of variance (ANOVA). Eq. (1) was used:

$$u_{\mathrm{bb}} = \sqrt{\frac{\boldsymbol{MS}_{\mathbf{among}} - \boldsymbol{MS}_{\mathrm{within}}}{\boldsymbol{n}}} \tag{1}$$

where

MS_{among}—mean of squared deviations between bottles;

MS_{within}—mean of squared deviations within bottles;

n—number of replicate sub-samples per bottle.

The calculated relative uncertainty component u_{bb} was 1.60%, resulting in an absolute contribution to the certified value of 0.192 mg/kg CN.

4. Stability Study

In December 2015, selected units of the bottled soil material were stored at temperatures of -20 °C, +20 °C, +40 °C and +60 °C, respectively (the indicated temperature values imply a tolerance of ±3 °C). After a storage time of 2, 4, 6, 9 and 12 months, respectively, two bottles per temperature level were analyzed in duplicate for their contents of total cyanide using (CFA) method according to ISO 17380 (with a sample intake of 5.0 g each) under repeatability conditions in one run with one calibration. The measurement results (see Appendix II) were evaluated by calculating the ratios R_t with Eq. (2) and their corresponding uncertainties u_t by Eq. (3):

$$R_t = X_t \,/\, X_{-20\ ^\circ\mathrm{C}} \tag{2}$$

$$u_t = (CV_t^{\,2} + CV^{2}_{-20\ ^\circ\mathrm{C}})^{1/2}\, R_t \tag{3}$$

where X_t and $X_{-20\ ^\circ\mathrm{C}}$ are the mean values of four analyses of samples stored at temperature t (+20 °C, +40 °C or +60 °C) and of samples stored at the reference temperature -20 °C, respectively. CV_t and $CV_{-20\ ^\circ\mathrm{C}}$ are the corresponding coefficients of variation. The results of this evaluation are given in Table 1.

Table 1 Results of the stability test after storage periods between 2 and 12 months.

Storage time	$R_t \pm u_t$ Samples stored at 20 °C
2 months	0.9963 ± 0.0188
4 months	1.0033 ± 0.0237
6 months	0.9910 ± 0.0125
9 months	0.9943 ± 0.0215
12 months	1.0011 ± 0.0286

Storage time	$R_t \pm u_t$ Samples stored at 40 °C
2 months	0.9784 ± 0.0141
4 months	0.9989 ± 0.0252
6 months	0.9402 ± 0.0126
9 months	1.0042 ± 0.0239
12 months	0.9976 ± 0.0349

Storage time	$R_t \pm u_t$ Samples stored at 60 °C
2 months	0.9042 ± 0.0144
4 months	0.8876 ± 0.0199
6 months	0.8494 ± 0.0276
9 months	0.8546 ± 0.0167
12 months	0.8440 ± 0.0234

If one postulates that the total cyanide mass fraction of samples stored at -20 °C does not change over time, in case of ideal sample stability at a higher storage temperature t the ratio R_t should be 1. In reality, however, unavoidable random variations of measurement results have to be taken into account. Thus, a material can be considered stable at storage temperature t if the value 1 is comprised between $R_t - u_t$ and $R_t + u_t$. This precondition is fulfilled for samples stored at a temperature of (20 ± 3) °C. On the other hand, for samples stored at 60 °C there is clear evidence for a nonnegligible degradation of complex cyanides leading to lower measurement results when determining total cyanide. Most likely this is due to the fact that volatile degradation products present in the headspace of the closed bottle can be lost when taking a sub-sample for analysis. In order to obtain an estimate for the long-term behavior of samples stored at different temperatures, an Arrhenius model was assumed for the dependence of the reaction (degradation) rate k_{eff} on storage temperature [4]. A plot of k_{eff} over the inverse temperature t (in K) is given in Fig. 1 (Appendix III).

Despite the apparent inadequacy of approximating the temperature dependence of k_{eff} by a straight line, this approach was used to get an estimate of the shelf life $\Delta_{\max}$ of the reference material for any storage temperature. The term "shelf life" herein refers to the period when degradation will presumably force the total cyanide content of the sample to fall below the certified lower expanded uncertainty limit. In the sense of a worst-case estimation, these calculations were carried out for the degradation rates at the upper confidence limit of the line shown in Fig. 1 according to Eq. (4):

$$\Delta_{\max} = \ln[(w_{\mathrm{cert}} - U_{\mathrm{cert}})/w_{\mathrm{cert}}]/k_{\mathrm{eff,upper}} \qquad (4)$$

with w_{cert} being the certified value of the total cyanide mass fraction and U_{cert} denoting its expanded uncertainty. Calculated estimates of shelf life for different storage temperatures are given in Table 2.

The data given in the Table 2 indicate a sufficient stability of samples stored at a typical room temperature of (20 ± 3) °C. However, any exposure to

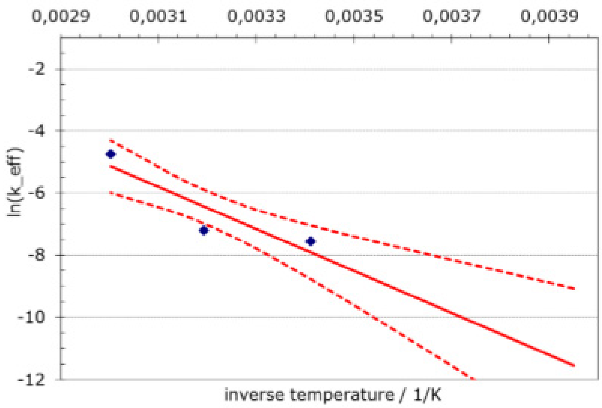

Fig. 1 Regression of total cyanide degradation rate k_{eff} over the inverse temperature and 95% one-sided confidence interval (Arrhenius plot).

Table 2 Shelf life of CRM BAM-U116/CGL306 at different storage temperatures.

Storage temperature	Shelf life (months)
-20 °C	600
+20 °C	79
+40 °C	25

the laboratory environment or higher temperatures may reduce the time of validity of the certified mass fraction of total cyanide. Therefore, an expiry date of two years beginning with the dispatch of the reference material from BAM or CGL is established. Stability testing will be continued by further measurements of units stored at -20 °C, +20 °C and +40 °C over the period of availability of the material. Thus, the validity of the expiry date of two years after dispatch given in the certificate is maintained by post-certification measurements performed at BAM.

5. Certification Study

5.1 Design of the Study

The certification study was organized as an ILC (Inter-Laboratory Comparison) and performed in March/April 2016. Each participant received one unit of the bottled candidate CRM and was asked to analyze four independent sub-samples. The determinations should be spread over two days, each time using freshly prepared calibrants. The information was provided that the total cyanide content of the soil sample was to be expected between 10 and 20 mg/kg. The analytical protocol prescribed by ISO 11262 had to be followed in full detail. For the determination of cyanide in the absorption solution, participating laboratories were requested to use the photometric method because of its better sensitivity and reproducibility compared to the titrimetric method. The photometric measurements should be carried out using calibration solutions prepared from a stock solution with a certified or at least verified cyanide concentration.

The dry mass content of the soil sample had to be determined on separate subsamples by drying to constant mass at (105 ± 2) °C according to ISO 11465 [5]. All analytical results of the participants were reported on this dry mass basis. Additionally, in order to identify potential “technical outliers” all participants had to analyze a control sample in the same manner as prescribed for the candidate CRM. The control sample (QC/GCN-2016) was a homogeneous soil material whose content of total cyanide had been determined in the course of a former PT (Proficiency Test) by 50 participants.

5.2 Participants

Besides BAM and CGL, a total of 14 German laboratories participated in the certification study on candidate CRM BAM-U116/CGL306. All of them were operating an internal quality management system accredited to ISO/IEC 17025 [6] and covering the determination of cyanide in soil. The strict observance of the requirements of ISO 11262 and of additional instructions given by BAM had been assured by all laboratories in advance. Participating laboratories in alphabetical order (not identical with the order of assigned laboratory code numbers):

AGROLAB Labor GmbH, Bruckberg (Germany)
ALS Analytik Labor Schirmacher GmbH, Hamburg (Germany);
BEGA.tec GmbH, Abteilung Labor, Berlin (Germany);
Bundesanstalt für Materialforschung und-prüfung (BAM), Division 1.6, Berlin (Germany);
Central Geological Laboratory (CLG), Department of Chemical and Physical Methods, Ulaanbaatar (Mongolia);
Chemlab-Gesellschaft für Analytik und Umweltberatung mbH, Bensheim (Germany)
Chemisches Labor Dr. Wirts + Partner, Sachverständigen GmbH, Hannover (Germany);
CLG Chemisches Labor Dr. Graser KG, Schonungen (Germany);
Eurofins Umwelt Ost GmbH, NL Freiberg, Bobritzsch-Hilbersdorf (Germany);
ICA-Institut für Chemische Analytik GmbH, Leipzig (Germany);
IHU-Geologie und Analytik, Gesellschaft für Ingenieur-, Hydro- und Umweltgeologie mbH, Stendal (Germany);

IUS Institut für Umweltanalytik und Schadstoffchemie GmbH, Stuttgart (Germany);

M&S Umweltprojekt GmbH, Labor Bad Muskau, Bad Muskau (Germany);

Umweltlabor ACB GmbH, Münster (Germany);

SGL Spezial-und Bergbau-Servicegesellschaft Lauchhammer mbH, Analytisches Labor, Lübbenau (Germany);

SGS Institut Fresenius GmbH, Herten (Germany).

5.3 Statistical Evaluation of Results

The measurement results obtained in the course of the inter-laboratory comparison are compiled in Appendix III. The bars in the graphic presentations indicate the standard deviations of individual laboratory's results. The bar associated with the mean of laboratory means M in Fig. 2 (Appendix III) represents the standard deviation of laboratory means. Further explanations are given in the notes to the respective graphs in Appendix III. In a first step, the results obtained for control sample QC/GCN-2016 were evaluated. Participants' results for the content of total cyanide in this sample had to fall within the specified tolerance range of (15.4 ± 1.94) mg/kg CN. The dataset of laboratory 04 did not fulfill this acceptance criterion and was considered as "technical outlier". As a consequence, the dataset of this participant for candidate CRM BAM-U116/CGL306 was also supposed as being biased and therefore excluded from further data processing. The same decision applies to the respective dataset of laboratory 15, because the sample intake for analysis of both the control sample and the candidate CRM was only 0.2 g. This was considered as a too severe deviation from the analytical protocol prescribed by ISO 11262.

Statistical tests and evaluation of the accepted results for candidate material BAM-U116/CGL306 were performed using software SoftCRM, version 1.2.2 [7].

The following tests were carried out at different significance levels α:

Scheffé's multiple *t*-test: All datasets compatible two-by-two?

Cochran test: Outlying variances?

Grubbs, Dixon and Nalimov tests: Outlying means?

Bartlett test: Variances homogeneous?

Snedecor *F*-test: Differences between datasets statistically significant?

Kolmogorov-Smirnov-Lilliefors test: Normality of the distribution of the means?

Skewness & Kurtosis test: Normality of the distribution of the means?

The results of these tests are summarized in Table 3.

As no technical reasons could be identified for "suspicious" dataset 13, all datasets were retained for further data processing.

6. Certified Value and Uncertainty

The unweighted mean of accepted laboratory means was considered as the best estimate w_{CN} for the value to be certified. It is expressed on a dry mass basis corresponding to a drying temperature of (105 ± 2) °C. When calculating the uncertainty of the certified mass fraction of total cyanide, the following contributions were taken into account:

u_{ILC}: uncertainty resulting from the inter laboratory comparison and representing the standard deviation of the mean of accepted dataset means

($u_{\mathrm{ILC}} = \mathrm{SD_M}/\sqrt{\mathrm{N}}$),

u_{bb}: uncertainty due to (a possible) hidden inhomogeneity of the material (see Clause 3),

u_{prec}: uncertainty reflecting the average precision of laboratory means. u_{prec} was calculated according to Eq. (5):

$$u_{\mathrm{prec}} = \sqrt{\sum_{i=1}^{N} SD_i^2 / nN} \qquad (5)$$

where SD_{i} is the standard deviation of the results of an individual participant, *N* is the number of accepted datasets, and *n* is the number of sub samples analyzed by each participant. The different contributions to the

Table 3 Results of statistical tests carried out on accepted participants' results.

Statistical test	Result of the test
Scheffé	Datasets differ significantly.
Cochran ($\alpha = 0.05$)	No outlying variances.
Cochran ($\alpha = 0.01$)	No outlying variances.
Grubbs ($\alpha = 0.05$)	No outlying laboratory means.
Grubbs ($\alpha = 0.01$)	No outlying laboratory means.
Dixon ($\alpha = 0.05$)	No outlying laboratory means.
Dixon ($\alpha = 0.01$)	No outlying laboratory means.
Nalimov ($\alpha = 0.05$)	Laboratory 13 is an outlier.
Nalimov ($\alpha = 0.01$)	No outlying laboratory means.
Bartlett ($\alpha = 0.05$)	Variances are homogeneous.
Bartlett ($\alpha = 0.01$)	Variances are homogeneous.
Snedecor ($\alpha = 0.05$)	Differences between datasets are statistically significant.
Snedecor ($\alpha = 0.01$)	Differences between datasets are statistically significant.
Kolmogorov-Smirnov-Lilliefors ($\alpha = 0.05$)	Based on the available data, the hypothesis of normality cannot be rejected.
Kolmogorov-Smirnov-Lilliefors ($\alpha = 0.01$)	Based on the available data, the hypothesis of normality cannot be rejected.
Skewness & Kurtosis ($\alpha = 0.05$)	Based on the available data, the hypothesis of normality cannot be rejected.
Skewness & Kurtosis ($\alpha = 0.01$)	Based on the available data, the hypothesis of normality cannot be rejected.
Pooling of individual data allowed?	No.

Table 4 Mass fraction and uncertainty components for total cyanide in CRM BAM-U116/CGL306.

Mass fraction w_{CN} (in mg/kg)	Uncertainty components (in mg/kg)			
	u_{ILC}	u_{bb}	u_{prec}	u_{com}
12.02	0.233	0.192	0.182	0.352

overall uncertainty of the certified mass fraction were combined according to GUM [8] using Eq. (6):

$$u_{com} = \sqrt{u_{ILC}^2 + u_{bb}^2 + u_{prec}^2} \tag{6}$$

The calculated mass fraction w_{CN} and the values of the different uncertainty components are given in Table 4.

The expanded uncertainty U was obtained by multiplying the combined uncertainty u_{com} by a coverage factor $k = 2$, giving a level of confidence of approximately 95% to be associated with the interval $\pm U$ around the certified mass fraction. After rounding the calculated numerical values, the certified mass fraction of total cyanide in CRM BAM-U116/CGL306 was assigned as (12.0 ± 0.8) mg/kg.

7. Traceability

It is important to note that the certified mass fraction of total cyanide in reference material BAM-U116/CGL306 is operationally-defined referring to the analytical protocol prescribed by ISO 11262:2011. The photometric determination of the liberated cyanide is traceable to the International System of Units (SI) via calibration using substances with certified analyte content.

8. Additional Material Data

The main matrix constituents of the bottled material were determined by WD-XRF (X-ray fluorescence) analysis giving the following non-certified results (Table 5).

Table 5 Non-certified results of elements for total cyanide in CRM BAM-U116/CGL306.

Element	Mass fraction (in %)
Si	35.6
Al	6.9
K	2.9
Na	2.5
Ca	0.8
Fe	0.8

Table 6 Informative analytical results of parameters for total cyanide in CRM BAM-U116/CGL306.

Parameter	Mass fraction (in %)	Analytical method
Dry mass content at 105 °C	99.8	ISO 11465 [5]
Loss on ignition at 550 °C	0.9	EN 15935 [9]
TC (Total Carbon)	0.2	ISO 10694 [10]

Further informative analytical results were obtained in the course of sample characterization (Table 6).

9. Information on the Proper Use of CRM BAM-U116/CGL306

9.1 Shelf Life

The initial stability study after storage of selected units at different temperatures did not reveal any statistically significant deterioration of the certified property if the bottled material is stored at a temperature below 25 °C. However, starting with dispatch of the material from BAM or CGL the validity of the certificate expires after two years. Post-certification measurements will be conducted in appropriate periods to keep this information up to date.

9.2 Transport, Storage and Use

CRM BAM-U116/CGL306 can be shipped at ambient temperature. Upon receipt the material has to be stored at a temperature below 25 °C in its original tightly closed bottle. Although the stability of the reference material is not affected by short periods of handling at ambient temperature, the bottle shall be left unclosed as short as possible. Care should be taken to avoid moisture pick up once the bottle is opened. The intended purpose of the reference material is the verification of analytical results obtained for the mass fraction of total cyanide in soils and soil-like materials applying the standardized procedure ISO 11262. As any reference material, it can also be used for routine performance checks (quality control charts) or validation studies. The material should be used as it is from the bottle. However, before taking a sub-sample a re-homogenisation by manual shaking of the closed bottle is strongly recommended. When determining the content of total cyanide, the analytical protocol prescribed by ISO 11262 must be followed. All analytical results have to be corrected for dry mass content of the material which should be determined according to ISO 11465 using a separate sub-sample. The value given in the Table 6 (99.8%) should be regarded as being indicative only.

9.3 Safety Instructions

No hazardous effect is to be expected when the material is used under conditions usually adopted for the analysis of environmental matrices moderately contaminated with cyanides. However, it is strongly recommended to handle and dispose the reference material in accordance with the guidelines for hazardous materials legally in force at the site of end use and disposal. It should be kept in mind that hydrogen cyanide and its salts are toxic. Therefore, caution should be exercised when manipulating cyanide-contaminated samples. Volatile hydrogen cyanide (with an odor of bitter almonds) is released from acidified solutions containing cyanide salts. As a minimum, all work shall be carried out in a fume hood.

9.4 Legal Notice

Neither BAM nor CGL, their contractors nor any person acting on their behalf:

(a) make any warranty or representation, express or imply, that the use of any information, material,

Table 7 The certified value and its uncertainty for total cyanide in CRM BAM-U116/CGL306.

Measurand	Mass fraction[a] in mg/kg	Uncertainty *U*[b] in mg/kg
Total cyanide according to ISO 11262:2011	12.0	0.8

[a] Unweighted mean value of 14 laboratory means which were corrected to the dry mass content of the material after drying to constant mass at (105 ± 2) °C.

[b] Estimated expanded uncertainty *U* with a coverage factor of $k = 2$, corresponding to a level of confidence of approximately 95% as defined in the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008).

apparatus, method or process disclosed in this document does not infringe any privately owned intellectual property rights; or

(b) assume any liability with respect to, or for damages resulting from, the use of any information, material, apparatus, method or process disclosed in this document save for loss or damage arising solely and directly from the negligence of BAM or CGL.

10. Summary

This report describes the certification of a reference material (CRM) for the determination of total cyanide in soil according to the analytical procedure prescribed by International Standard ISO 11262:2011. The intended purpose of CRM BAM-U116/CGL306 is the verification of analytical results obtained for the mass fraction of total cyanide in soils and soil-like materials applying the standardized procedure ISO 11262:2011. As any reference material, it can also be used for routine performance checks (quality control charts) or validation studies (Table 7).

CRM BAM-U116/CGL306 is available as a powder with particle sizes below 125 µm and is supplied in 100 mL plastic (HDPE) containers containing (100 ± 3) g. The minimum amount of sample to be used for the determination of total cyanide is 5 g.

The certified value is valid for a period of two years beginning with the dispatch of the reference material from BAM or CGL.

References

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[10] International Organization for Standardization. 1995. “Soil Quality-Determination of Organic and Total Carbon after Dry Combustion (Elementary Analysis).” ISO 10694:1995.

Annexes

Appendix I:	Homogeneity study (measurement results)
Appendix II:	Stability study (measurement results)
Appendix III:	Certification study (measurement results of participants)

List of used abbreviations

(if not explained elsewhere in the report)

M : arithmetic mean of means;

N : number of individual datasets;

SD_i : standard deviation of an individual dataset;

SD_M : standard deviation of the mean of dataset means.

Appendix I

Homogeneity study (measurement results).

Total cyanide;

Sample intake: 5.0 g;

Analytical method: ISO 17380:2013.

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
003	11.02	11.09	11.29	11.13	0.140
088	11.24	11.47	11.69	11.47	0.225
146	11.24	11.09	11.18	11.17	0.075
214	11.64	11.63	11.35	11.54	0.165
267	11.30	11.41	11.49	11.40	0.095
319	11.35	10.87	11.40	11.21	0.293
358	11.05	11.17	11.48	11.23	0.222
447	11.64	11.48	11.84	11.65	0.180
522	11.64	11.78	11.82	11.75	0.095
609	11.65	11.48	10.93	11.35	0.376
699	11.58	11.36	11.22	11.39	0.181
786	11.46	11.52	11.86	11.61	0.216
864	11.93	11.77	11.77	11.82	0.092
911	11.12	11.46	11.44	11.34	0.191
955	11.65	11.48	11.75	11.63	0.137

M (mg/kg): 11.45;
SD_M (mg/kg): 0.215;
u_{bb} (% rel.): 1.60;
(acc. to ISO Guide 35).

Appendix II

Stability study (measurement results). Total cyanide

Sample intake: 5.0 g;

Analytical method: ISO 17380:2013.

Sample I.D.	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	11.34	11.31	11.43	11.21	11.32	0.091
	+20 °C	11.09	11.15	11.50	11.38	11.28	0.193
	+40 °C	10.92	11.23	11.03	11.13	11.08	0.133
	+60 °C	10.30	10.03	10.34	10.28	10.24	0.141
4 months	-20 °C	10.94	11.28	11.38	11.50	11.28	0.241
	+20 °C	11.23	11.21	11.36	11.45	11.31	0.113
	+40 °C	11.14	11.25	11.48	11.18	11.26	0.152
	+60 °C	10.10	9.94	9.99	10.00	10.01	0.067
6 months	-20 °C	11.17	11.40	11.40	11.38	11.34	0.112
	+20 °C	11.15	11.17	11.32	11.30	11.24	0.087
	+40 °C	10.60	10.65	10.59	10.80	10.66	0.097
	+60 °C	9.76	9.72	9.85	9.19	9.63	0.298
9 months	-20 °C	11.17	11.36	11.28	11.52	11.33	0.147
	+20 °C	11.08	11.13	11.37	11.49	11.27	0.195
	+40 °C	11.61	11.51	11.10	11.30	11.38	0.227
	+60 °C	9.83	9.75	9.66	9.50	9.69	0.142
12 months	-20 °C	11.21	10.99	11.53	11.45	11.30	0.245
	+20 °C	11.19	11.08	11.42	11.54	11.31	0.210
	+40 °C	11.25	11.68	10.93	11.21	11.27	0.310
	+60 °C	9.37	9.66	9.69	9.41	9.53	0.166

Appendix III

Table 1 Certification inter-laboratory comparison. **Total cyanide**

Measurement results for control sample QC/GCN-2016

Analytical method: ISO 11262:2011

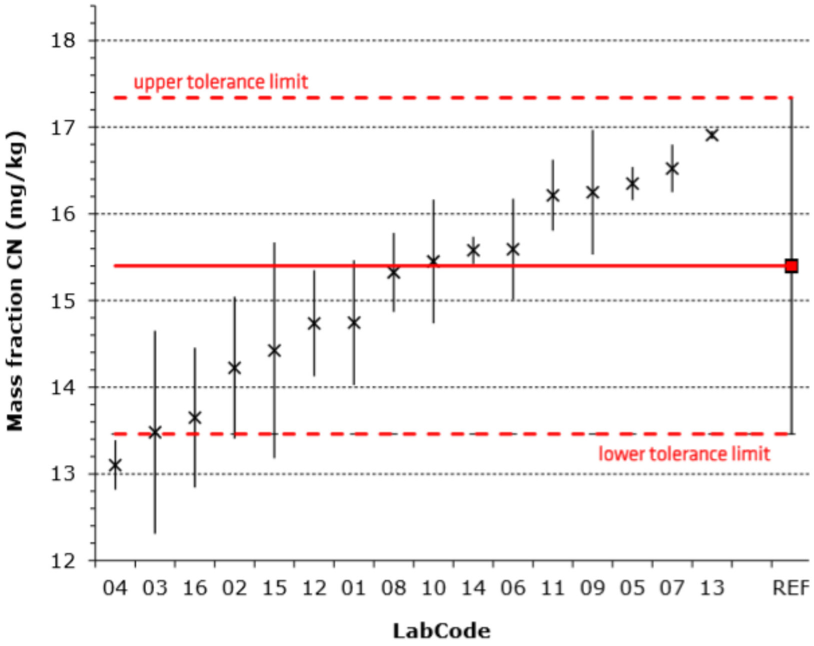
LabCode	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
04	12.77	13.22	13.43	12.99	13.10	0.29
03	14.63	13.52	12.29		13.48	1.17
16	13.7	12.5	14.3	14.1	13.65	0.81
02	14.6	15.0	13.1	14.2	14.23	0.82
15	14.9	12.6	14.8	15.4	14.43	1.24
12	13.97	14.68	14.84	15.46	14.74	0.61
01	13.97	14.32	15.51	15.18	14.75	0.72
08	15.84	14.76	15.21	15.49	15.33	0.46
10	15.0	15.9	16.2	14.7	15.45	0.71
14	15.53	15.62	15.77	15.4	15.58	0.16
06	16.16	16.03	15.07	15.11	15.59	0.58
11	16.28	15.65	16.63	16.3	16.22	0.41
09	17.3	16.1	15.7	15.9	16.25	0.72
05	16.2	16.4	16.6	16.2	16.35	0.19
07	16.8	16.7	16.4	16.2	16.53	0.28
13	16.84	16.94	16.93	16.93	16.91	0.05

M (mg/kg): 15.16; SD_M (mg/kg): 1.161; RSD (%): 7.66.

Appendix III

Fig. 1. Certification inter-laboratory comparison. Total cyanide

Measurement results for control sample QC/GCN-2016



Control sample QC/GCN-2016 was a homogeneous soil material whose content of total cyanide had been determined in the course of a former PT by 50 participants.

The robust PT-mean (data analysis according to ISO 5725-5) was 15.4 mg/kg CN, being the assigned value REF for assessment of the technical performance of laboratories participating in the certification inter-laboratory comparison.

The tolerance limits for the results obtained for control sample QC/GCN-2016 were set to REF ± SR, where SR is the reproducibility standard deviation of the PT-results (SR = 1.94 mg/kg CN).

Appendix III

Table 2 Certification inter-laboratory comparison. Total cyanide

Measurement results for candidate CRM BAM-U116/CGL306 (all datasets)

Analytical method: ISO 11262:2011

LabCode	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
04	9.95	8.65	9.43	9.49	9.38	0.54
01	11.03	10.60	10.40	11.08	10.78	0.33
15	12.2	10.5	10.5	10.2	10.85	0.91
03	11.20	10.74	10.54	11.04	10.88	0.30
02	10.3	10.8	11.8	11.5	11.10	0.68
12	11.16	11.02	11.21	11.49	11.22	0.20
08	11.91	11.37	11.98	11.66	11.73	0.28
14	12.00	12.05	12.02	11.41	11.87	0.31
09	12.4	11.8	11.9	11.5	11.90	0.37
06	11.99	11.94	11.99	11.91	11.96	0.04
05	12.4	12.7	11.9	12.1	12.28	0.35

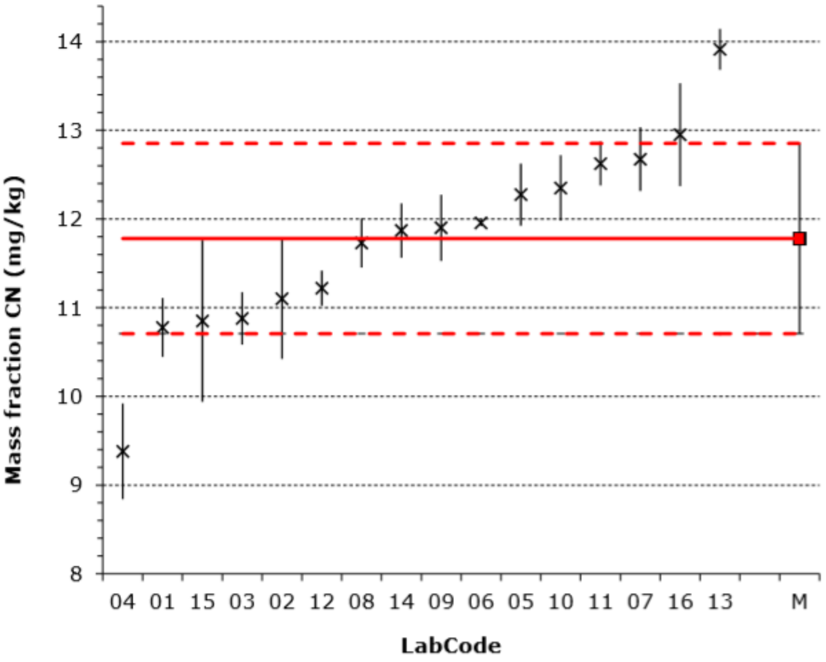
10	11.9	12.8	12.3	12.4	12.35	0.37
11	12.47	12.41	12.66	12.96	12.63	0.25
07	13.0	12.9	12.6	12.2	12.68	0.36
16	13.6	12.2	12.9	13.1	12.95	0.58
13	14.05	14.05	13.98	13.57	13.91	0.23

M (mg/kg): 11.78; SD_M (mg/kg): 1.073; RSD (%): 9.11.

Appendix III

Fig. 2. Certification inter-laboratory comparison. Total cyanide

Measurement results for candidate CRM BAM-U116/CGL306 (all datasets).



The dataset of laboratory 04 was considered as a technical outlier and excluded from further data processing because the mean result of this participant for control sample QC/GCN-2016 was outside the tolerance limits.

The dataset of laboratory 15 was excluded from further data processing because the sample intake for analysis was only 0.2 g (!!). This was considered as a too severe deviation from the analytical protocol prescribed by ISO 11262:2011.

Appendix III

Table 3 Certification inter-laboratory comparison. Total cyanide

Measurement results for candidate CRM BAM-U116/CGL306 (accepted datasets)

AM: ISO 11262:2011

LabCode	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
01	11.03	10.60	10.40	11.08	10.78	0.33
03	11.20	10.74	10.54	11.04	10.88	0.30
02	10.3	10.8	11.8	11.5	11.10	0.68
12	11.16	11.02	11.21	11.49	11.22	0.20
08	11.91	11.37	11.98	11.66	11.73	0.28
14	12.00	12.05	12.02	11.41	11.87	0.31

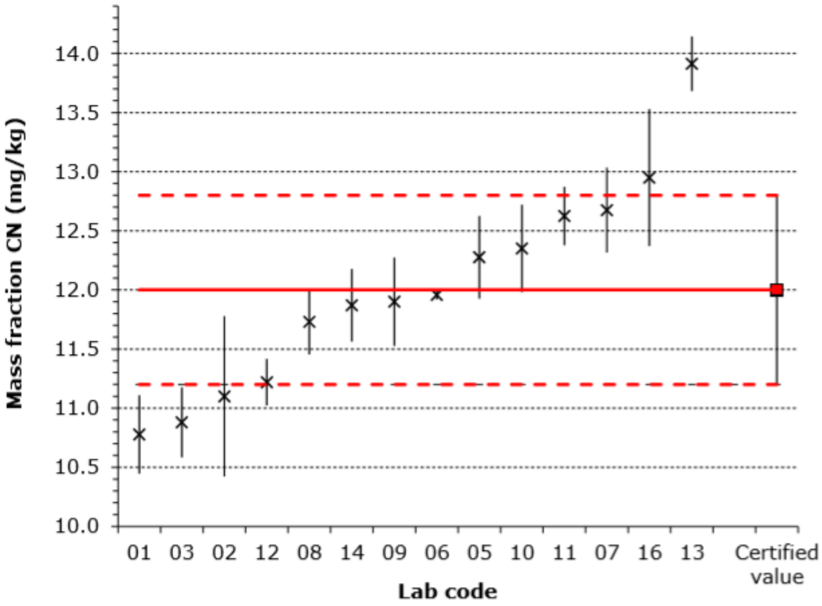
09	12.4	11.8	11.9	11.5	11.90	0.37
06	11.99	11.94	11.99	11.91	11.96	0.04
05	12.4	12.7	11.9	12.1	12.28	0.35
10	11.9	12.8	12.3	12.4	12.35	0.37
11	12.47	12.41	12.66	12.96	12.63	0.25
07	13.0	12.9	12.6	12.2	12.68	0.36
16	13.6	12.2	12.9	13.1	12.95	0.58
13	14.05	14.05	13.98	13.57	13.91	0.23

M (mg/kg): 12.02; SD_M (mg/kg): 0.871; RSD (%): 7.25.

Appendix III

Fig. 3. Certification inter-laboratory comparison. Total cyanide

Measurement results for candidate CRM BAM-U116/CGL306 (accepted datasets)



The bar associated with the plotted certified value represents its expanded uncertainty *U*.

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Evaluation of Industrial Pollution by Means of Experimental Economics

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Abstract: In this work, a methodological framework under the form of an algorithmic procedure, including 28 activity stages and 6 decision nodes, has been developed for evaluating environmental impact caused by industrial activities. The main part of this procedure is a modification of the CVM (Contingent Valuation Method), which is heavily relied on survey-based estimation of WTP-WTA (Willingness To Pay/Accept, respectively). The survey may take place either under a strictly controlled environment or in situ and as-is ("laboratory conditions" or "field conditions", respectively, in the terminology of experimental economics). Implementation of this methodology is presented, referring to three cases of industrial pollution (in three different sites) caused by: (i) a cement producing unit, (ii) an oil refinery complex, and (iii) an industrialized small city with an intensively polluted port, where several industrial units co-exist, all of them located in the vicinity of Athens, Greece. The results are interpreted/discussed and conclusions are drawn.

Key words: Environmental impact, WTP, WTA, industry relocation.

1. Introduction

During the last three decades, there has been growing interest in developing methods for assessing the preferences (of experts, stake holders, community/organization members, independent individuals) for environmental quality [1]. Among them, the CVM (Contingent Valuation Method) is frequently applied to: (i) economic valuation of environmental projects or works/activities (planned or in operation) with a significant environmental impact and (ii) damage assessment after environmental accidents, i.e., after incidents that deteriorate environmental quality [2]. This method is heavily relied on survey-based estimation of: (i) WTP (Willingness To Pay), which is the maximum amount of money a person, would be willing to pay, sacrifice or exchange for a good, and (ii) WTA (Willingness To Accept), which is the minimum amount of money a person would be willing to accept in order to abandon a good. WTP is bounded by income while WTA is potentially unlimited [3].

Whether WTP or WTA is appropriate, depends on the prior distribution of property rights and the direction of change under consideration [4, 5]. The current endowment of an environmental commodity is often taken as implying legal right to an increase in the quantity of an environmental amenity and should be valued using WTP whereas reductions should be valued using WTA [6, 7]. If WTP and WTA were evaluated at the same level of utility, they should be identical, but empirical evidence consistently demonstrates that WTA may exceed WTP by an order of magnitude [8, 9].

The aim of this work is to present a dynamic methodological framework for evaluating environmental impact caused by industrial activities by means of the CVM, referring to alternative routes of investigation and including successive levels of information granularity in continuous interaction with a dedicated local KB (Knowledge Base) created ad hoc. Results from three case studies are also presented [10].

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2. Methodology

For the purposes mentioned above, authors have designed/developed the following methodological framework under the form of an algorithmic procedure, including 28 activity stages and 6 decision nodes (for their interconnection, see Fig. 1).

(1) Description of the domain under consideration by means of a GIS (Geographical Information System), including separate layers for the spatial distribution of the relevant parameter values, like industrial activity, roads network, commercial activity, permanent and transient (due to tourism) population, waterbodies and pollution.

(2) Description of the environmental project to be evaluated.

(3) Selection of permanent population characteristics, putting emphasis on the economic parameters necessary to estimate the various kinds of elasticity.

(4) Stratification of population, according to the characteristics selected in (3).

(5) Collection of feasible scenarios about improving environmental quality.

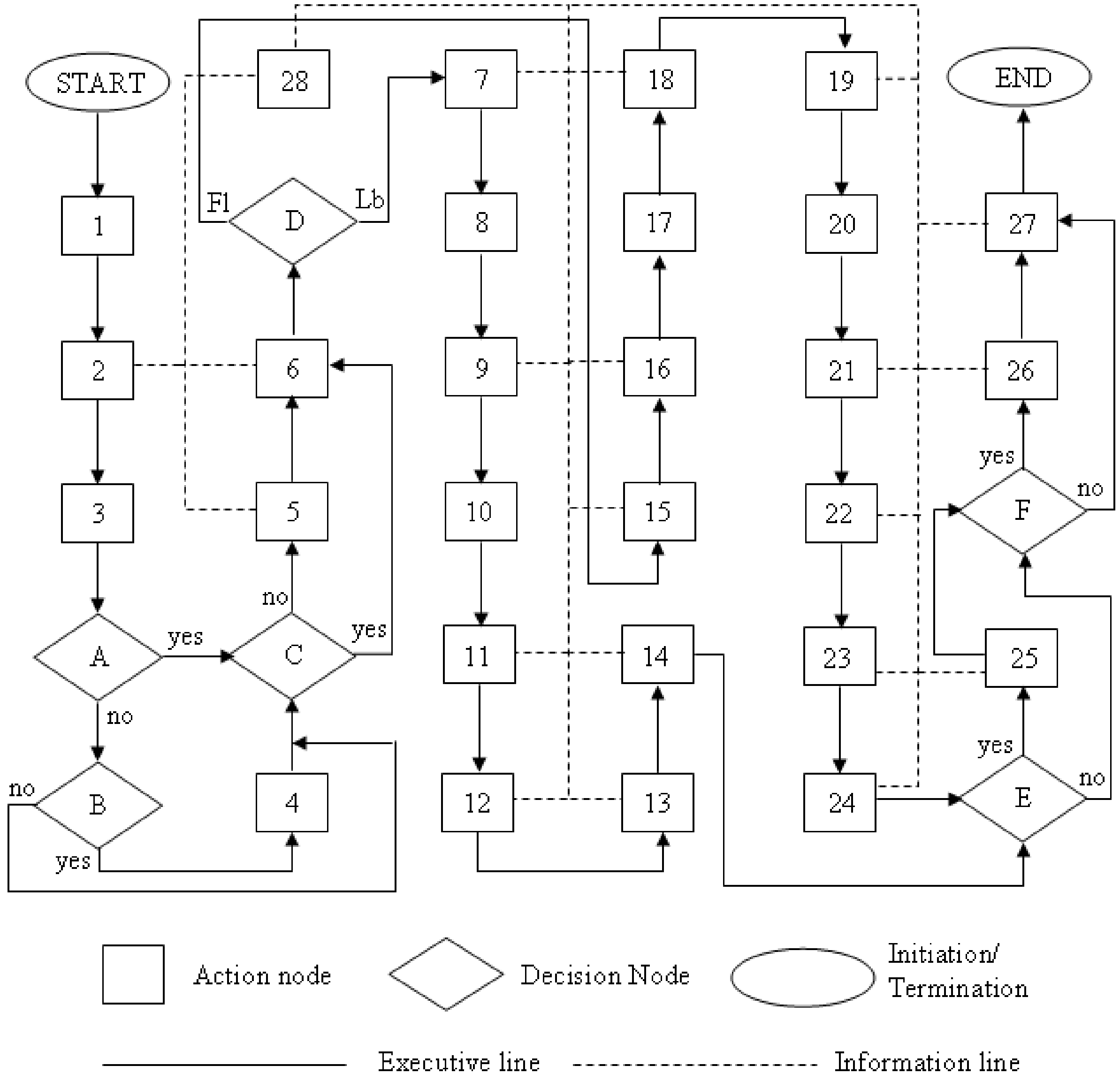

Fig. 1 The methodological framework, under the form of an algorithmic procedure, developed for evaluating environmental impact caused by industrial activities.

(6) Multicriteria choice of the most realistic/promising scenario.

(7) Design of the CVM questionnaire.

(8) Sample selection, according to the stratification performed in (4).

(9) Training of the interviewees participating in the evaluation.

(10) Communication/cooperation with the interviewees to obtain reliable answers to the Lb-questionnaire.

(11) Processing of the data obtained in the responses to the Lb-questionnaire.

(12) Conclusions covering the various entities of the Lb-questionnaire.

(13) Circulation of a post-CVM questionnaire to obtain information about the functionality of the method itself.

(14) Multifaceted/holistic conclusions.

(15) Design of Fl-questionnaire.

(16) Preparation of supporting material for interviewees' training.

(17) Intermediate circulation of the basic questionnaire among the respondents (small/medium sample size) to obtain information at a lower granularity level.

(18) Processing of the data obtained in the responses to the basic Fl-questionnaire.

(19) Basic conclusions and final formulation of the questionnaire.

(20) Final circulation of the refined/detailed questionnaire among the respondents (medium/large sample size) to obtain information at a higher granularity level.

(21) Processing of the data obtained in the responses to the refined/detailed Fl-questionnaire.

(22) Conclusions covering the various entities of the Fl-questionnaire.

(23) Circulation of a post-CVM questionnaire to obtain information about the functionality of the method itself.

(24) Multifaceted/holistic conclusions.

(25) Synthesis of results obtained herein with information extracted from similar cases.

(26) Meta-analysis, including comparison of methods.

(27) Proposals for environmental policymaking.

(28) Creation/operation/enrichment/updating of a KB, to cover the needs of the current work; searching within external bases by means of an IA (Intelligent Agent), as that described in Ref. [4].

- Do the interviewees form a homogenous set?
- Is stratification and corresponding sampling feasible?
- Are these estimates of income elasticity (as regards expenses for improving/sustaining environmental quality) available?
- Will the survey take place within a strictly controlled environment or *in situ* and "as-is" ("laboratory conditions" and "field conditions", respectively, in the terminology of experimental economics, quoted as Lb and Fl in Fig. 1)?
- Is there additional endogenous (already processed/stored in the KB) information extracted from similar cases?
- Is there additional exogenous information extracted from similar cases found in external KBs by means of the IA of stage 28?

3. Results and Discussion

The methodological framework described above has been implemented in three cases at sites close to Athens (Lat. 37°58′42.22″ N, Long. 23°43′01.12″ E), referring to (i) the towns/ports Agioi Theodoroi (50.94 km south of Athens, Lat. 37°55′44.55″ N, Long. 23°08′25.96″ E) and Khalkis (54.87 km north of Athens, Lat. 38°27′47.06″ N, Long. 23°35′29.78″ E), where the source of pollution is an oil refinery and a cement production unit, respectively, and (ii) the small industrial city/port (actually a suburb 18.04 km to the south of Athens) of Eleusina (Lat. 38°0.2′36.09″ N, Long. 23°32′31.63″ E), where there are several sources of pollution.

In the town of Agioi Theodoroi, a quarter of the interviewees behave in an absolutely passive mode, while the rest exhibit a consistent attitude willing to pay or accept a rather small amount of money; nevertheless, 35% of them are in favor of relocation, possibly because they have interests in real estate or business associated with tourism.

In the town of Khalkis, although 37% of the interviewees are not willing to pay, the corresponding percentage for WTA is negligible while the rest WTA-percentages are considerably high and in good agreement with the results for WTR.

In the small city of Eleusina, the absolutely passive percentage is quite high for both, WTP and WTA (46% and 67%, respectively), but 47% of the interviewees are in favor of relocation; this can be attributed to the high price of land in this suburb of Athens; the interviewees think they can take advantage from changing the use of land from industrial to urban, while they believe that the industrial units, where most of the inhabitants work, will relocate to a nearby place, quite accessible without entailing excessive transportation cost.

4. Conclusion

The functionality of the methodological framework, developed under the form of an algorithmic procedure including 28 activity stages and 3 decision nodes, for evaluating environmental impact caused by industrial activities was proved by applying it to three cases at sites close to Athens, referring to (i) the towns/ports Agioi Theodoroi (50.94 km south of Athens) and Khalkis (54.87 km north of Athens), where the source of pollution is an oil refinery and a cement production unit, respectively, and (ii) the small industrial city/port (actually a suburb 18.04 km to the south of Athens) of Eleusina, where there are several sources of pollution.

Certain results presented herein give reasonable implications between WTP, WTA, WTR, although the absolute monetary magnitudes between WTP and WTA as well as their ratio differ significantly from what is quoted in technical literature; the relatively high percentage of interviewees answering in favour of the relocation of the polluting industrial units can be attributed to their belief that they can take advantage from changing the use of land from industrial to urban, while they think that the industrial units, where most of the inhabitants work, will relocate to a nearby place, quite accessible without entailing excessive transportation cost.

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