Natural and artificial radionuclides in sludge, sand, granular activated carbon and reverse osmosis brine from a metropolitan Drinking Water Treatment Plant

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1.Introduction

Water resources usually need treatment prior to human consumption as it may contain particles, chemical substances or pathogens that can make it unsafe. Specific treatments are applied to improve water quality and different technologies are currently used in order to guarantee a good enough standard of the drinking water supply. The amount of natural radionuclides dissolved in raw water mainly depends on the specific activities of radionuclides in rocks and soils as well as subsequent interactions between water and rocks. However, radionuclides can also be present attached to particulates or in the form of colloids (Chabaux et al., 2008). Naturally occurring radionuclides consist of primordial nuclides (mainly ^{238}U, ^{235}U, ^{232}Th decay chains and ^{40}K), as well as cosmogenic nuclides such as ^{7}Be, ^{3}H and ^{14}C. Anthropogenic radionuclides such as ^{60}Co, ^{90}Sr, ^{137}Cs or $^{239/240}Pu$ may also be present due to nuclear weapons tests carried out in the atmosphere or accidents at nuclear power plants, while radionuclides such as ^{99m}Tc or ^{131}I are used in medical applications and can be found in surface waters or sediments (Fischer et al., 2015, 2009; Rose et al., 2013). Thus, depending on water flow characteristics and water treatment technology, radionuclides will be removed from the water and will accumulate in by-products and other materials.

Extensive research has been devoted to radioactivity content in water, as in (Desideri et al., 2007; Karamanis et al., 2008), and how to reduce it (Baeza et al., 2006; Montaña et al., 2013). Conventional drinking water treatment plants (DWTPs) have a fairly standard sequence of processes which essentially consist of solid separation using physical processes such as coagulation, flocculation, filtration and settling, together with chemical processes such as oxidation and final disinfection. In the review (Fonollosa et al., 2014), the authors highlighted the fact that the radioactivity content in sludge, mainly of a natural origin, is highly variable from plant to plant, depending on the characteristics of the raw water and also on the treatment followed by the plant. Consequently, the radiological risk of such sludge also depends on these factors. In addition, it should be pointed out that most of the previous studies do not provide information on the variability of the radioactivity content in DWTP sludges generated by the plants.

Despite studies done in this field, at present information available on the radioactivity content in filtering materials and other by-products routinely generated in the purification process in full-scale DWTPs is still scarce and studies have been done on plants with low-medium water treatment capacity (<1000-94043 population)(Kleinschmidt and Akber, 2008). Furthermore, there is no available prior published information which deals with the presence of biomedical radionuclides in DWTP by-products and materials. Therefore, this study aims to provide novel information on the radioactivity content in by-products and different filtering materials from a large-scale Metropolitan DWTP that treats both surface water and groundwater.

Evaluation of risk management of wastes containing natural and/or man-made radionuclides and their disposal is a matter of interest, since when the predicted exposure is not certain to be trivial, their disposal or re-use should be authorized depending on the regulatory requirements of each country. As regards naturally occurring radioactive materials (known as NORM), there are some studies related to different industries including water treatment, e.g. the petroleum or mineral industry (Mora et al., 2016; Pontedeiro et al., 2007; Smith et al., 2003). As regards artificial radionuclides in DWTPs, available studies are focused on post-accident scenarios (Jeong et al., 2014; Park et al., 2015) and do not deal with operational routines.

This work will contribute to the current knowledge in this field by providing data on both natural and biomedical radionuclides. From a mid-term sampling campaign over six years, the radiological risk of the studied materials will be assessed by applying current international recommendations (EC, 2013; IAEA, 2004).

2. Raw water and DWTP characteristics

The plant under investigation supplies the Barcelona Metropolitan area (more than 3200000 inhabitants) with a maximum capacity of 5.3 $m^3 \cdot s^{-1}$. For the period 2007-2014 the plant supplied the distribution network with 74-100·10^6 $m^3 \cdot y^{-1}$, which represents 30-50% of the annual basis of the water for human consumption in the Metropolitan area. The Llobregat River (LR) is the main source of raw water for the plant; however, sometimes the plant is supplied with wells.

The surface water catchment area is located in the low LR basin close to the DWTP with a median flow rate of 6.7 $m^3 \cdot s^{-1}$. Characteristics of the Llobregat river water are shown in Table 1. Most of the gross beta activity corresponds to ^{40}K, due to the relatively high potassium and salinity concentration of the LR because of NORM mining activity and geological formations of evaporite-bearing materials in the upper-middle basin of the river (Fernández-Turiel et al., 2003). The total uranium activity in the LR basin was also studied and the mean activity at the collection point was found to be 0.060 $Bq \cdot L^{-1}$(Camacho et al., 2010). The middle and low river basins are both urban and industrial and receives effluents from waste water treatment plants.

Wells are used mainly in periods of drought or on isolated days when the river flow rate is low. They are also used when episodes of river water pollution prevent water extraction or when water quality fails to reach the water company's specifications. The wellsare located on the Vall Baixa Sedimentary Aquifer, in particular in the area known as Cornellà. The aquifer is recharged mainly by natural infiltration from LR (ACA 2005) and ^{40}K is the main contributor to the beta activity of aquifer water (Table 1).

Treatment at the Metropolitan DWTP (Fig. 1.) is based on physical removal of particles and elimination of dissolved compounds and is detailed as follows.

Particle removal, only used for LR surface water: after chlorination and addition of coagulants, most of the particles are removed from the influent in static coned-shaped decanters where the water flows upwards. Sand bed filtration is applied after coagulation for final clarification. The sludge from decanters, after thickening, sieving, dehydrating, addition of NaOH and atomizing (500°C) is obtained as 150 µm dry particles. About 3,500 tonnes of atomized sludge are generated each year.

Dissolved compound removal: after groundwater is taken into the plant, the flow is divided into two treatment lines. In the first one, ozonization is carried out before granular active carbon (GAC) bed filtration (3000 m^3 of carbon installed). In order to reinforce the plant facilities a second parallel line was installed in 2009 where the water flow passes through ultrafiltration (UF) and reverse osmosis (RO) membranes which produce $6 \cdot 10^6$ m^3 RO brine per year.

3. Methodology

3.1. Sampling

During the period 2007-2014 15 sludge, 4 sand, 22 granulated activated carbon (GAC) and 3 reverse osmosis (RO) brine samples were taken at the DWTP (sampling points are indicated in Fig. 1). The plant materials were collected using 3L and 1L polyethylene containers for liquid and solid samples, respectively and transferred to the Radioactivity Analysis Laboratory. The sludge was sampled over two time periods (2007-09 and 2012-14) at least twice a year, for the dehydration and atomization steps, while the filtering sands were collected once a year at three different sites of the filtering area. Furthermore, one sample of "virgin" sand was analyzed.

GAC samples were collected at different stages during their usage cycle. Once the material reaches the plant, the adsorption capacity of the GACs is monitored by means of the iodine index (milligrams of adsorbed iodine per gram of carbon (ASTM, 2014)). The GAC is used until their efficiency is significantly reduced. At this stage the GAC is regenerated in industrial ovens by pyrolysis and is subsequently returned to the plant to be re-used (Fig. 2). After some regeneration cycles the GAC must be substituted by virgin material. Different samples were therefore collected: "Virgin" GAC: 3 samples; random sampled "In-use" GAC (with iodine indexes between 484-805): 10 samples; "exhausted" GAC (iodine index less than 530): 4 samples, and just "regenerated" GAC: 5 samples.

3.2 Sample pre-treatment and analysis

Long–lived radionuclides in solid samples were measured after being homogenized and dried in an ovenat 105°C until a constant weight. The different solid materials analyzed were wrapped with polytetrafluoroethylene thread seal tape (0.2mm) in a 100 mL polyethylene jar for at least 20 days to avoid ^{222}Rn leaks and reach the secular equilibrium between the ^{226}Ra daughters. Liquid samples were poured into a 400 mL Marinelli beaker and also sealed for at least 20 days. In order to be able to detect the short-lived ^{131}I, 52% of the samples (n=22 including sludge, sands and GACs) were also measured in wet weight in a 100 mL polyethylene jar after a short period of time of 1-10 days after sampling.

Measurements were done by gamma spectrometry using two Canberra hyperpure germanium (HPGe) coaxial detectors, models GX4020 and GX3020. The GX4020 detector is equipped with a end cap with a Carbon Epoxy window, while the GX3020 detector has a end cap with a Be window. The detectors were located in a room with 1-m-thick walls, and were shielded with 10.5 cm of lead plus 2 mm of copper (GX4020 detector), and 14.4 cm of iron (GX3020 detector). Their relative efficiencies were 41 % and 33 % respectively, and the resolutions were 1.86 and 1.77 keV at 1.33 MeV of ^{60}Co. The mixed-gamma-ray standard solution cointaining ^{57}Co, ^{60}Co, ^{88}Y, ^{109}Cd, ^{113}Sn, ^{137}Cs, ^{139}Ce and ^{241}Am (59.5-1332.5 keV energy range) was spiked in matrices with different densities, poured into the geometries and measured in both HPGe detectors. Afterwards, the mean full energy peak efficiency in each case was calculated as a function of the gamma-ray energy measured, generating a logarithmic polynomial fit for the spectra. Genie 2000© software (Canberra Industries, Meriden, USA) was used for the gamma spectra analysis.

^{7}Be, ^{40}K , ^{137}Cs, ^{210}Pb and ^{131}I activities were determined through the 477.6, 1460.7, 661.7 46.5 and 364.5 keV gamma lines respectively. The activities of some natural radionuclides were measured assuming they were in secular equilibrium with their descendants: ^{238}U was determined through ^{234}Th (63.3 keV gamma line), ^{226}Ra through ^{214}Pb (351.9 keV gamma line), ^{228}Ra through ^{228}Ac (991.3 keV gamma line) and ^{228}Th through ^{212}Pb (238.7 keV gamma line). The acquisition times ranged from 1 to 5 days for natural radionuclides and from 5 hours to 4 days for ^{131}I.

All reported uncertainties correspond to the combined expanded uncertainty (coverage factor, k=2) where the net peak area quantification and the detection efficiency are the main sources of uncertainty. All the procedures were validated following the quality requirements of the ISO/IEC 17025:2005 standard (ISO/IEC, 2010).

3.3 Risk assessment

As regards the sludge generated in a DWTP, its re-use for different applications in Spain such as additives in the cement industry (Rodríguez et al., 2010) or as ceramic bricks (Torres et al., 2012) have been considered in recent years. Therefore, the risk associated with their use in building materials has been evaluated.

The Euratom 2013/59 Directive (EC, 2013) establishes reference levels for indoor gamma radiation emitted from building materials, and defines the activity concentration index (I) that should be used:

$$I = C^{226}Ra/300\ Bq\cdot kg^{-1} + C^{232}Th/200\ Bq\cdot kg^{-1} + C^{40}K/3000\ Bq\cdot kg^{-1} \quad (1)$$

where C is the specific acitivity of the corresponding radionuclide in $Bq\cdot kg^{-1}$ in the building material. In the case of ^{232}Th, its daughter ^{228}Ra concetration is also considered equal (EC, 2013) and used in the present study.

The index relates to the gamma radiation dose, in excess of typical outdoor exposure, in a building constructed from a specified building material. Although the index applies to the building material and not to its constituents, it could be used as a preliminary conservative approach. A index value of $I\geq1$ might result in the reference level of 1 mSv per year (indoor external exposure to gamma radiation emitted by building materials, in addition to outdoor external exposure) being exceeded.

The radiological risk of the studied materials has also been assessed by comparison of the obtained concentration values with the exemption levels proposed by the IAEA (2004), and which have been adopted by the European Commission in the Euratom Directive 2013/59 (EC, 2013). Doses to individuals as a consequence of specific activities below these levels would be unlikely to exceed about 1 mSv per year.

In terms of natural radionuclides the exemption level for ^{40}K is 10 $kBq\cdot kg^{-1}$, whereas it is 1 $kBq\cdot kg^{-1}$ for all other radionuclides. For ^{131}I (radionuclides of an artificial origin), the exemption value by default to any amount and to any type of solid material is 10 $kBq\cdot kg^{-1}$. The exemption values for the specific activities in moderate amounts of any type of material are not applicable in our case since moderate quantities would mean of the order of one tonne of material.

4. Results and discussion

4.1 Long-lived radionuclides

Specific activities in dry weight of natural nuclides from the ^{238}U decay chain (^{238}U, ^{226}Ra, ^{210}Pb), the ^{232}Th decay chain (^{228}Ra, ^{228}Th), and also ^{40}K, cosmogenic ^{7}Be and artificial ^{137}Cs were determined in sludges (Fig. 3), sands, GACs and RO brines (Tables 2 and 3).

4.1.1 Sludge

The results in terms of activities in dry weight are shown in Fig. 3. as boxplots.

^{238}U decay chain

Sludges showed a ^{238}U median concentration value of 47Bq·kg^{-1} and a range of results between 33-88 Bq·kg^{-1} with a relative standard deviation (RSD %) of 30%. For ^{226}Ra (RSD=17%) the obtained median specific activity (29Bq·kg^{-1}) was slightly lower than for ^{238}U and the results ranged within 18-35 Bq·kg^{-1}. Furthermore, variability of ^{226}Ra in the studied plant is also much lower than the RSD of 69% found for its short-lived daughter nuclide ^{214}Pb in the sludges from an Ebro River DWTP (Palomo et al., 2010a). ^{210}Pb has shown similar results to those obtained for ^{238}U with an interval of 39-85 Bq·kg^{-1} and a mean value of 55Bq·kg^{-1} (RSD=20%). The results are in agreement with those reported in South East Queensland, Australia (^{238}U: 30-250 ^{226}Ra: 6-120 ^{210}Pb 10-110 Bq·kg^{-1} dry weight;Kleinschmidt and Akber, 2008) and also with the wide range of results reported in the Fonollosa et al. (2014) review.

The results indicate that ^{238}U and ^{226}Ra are not in secular equilibrium in the studied sludge, specifically the mean ^{238}U/^{226}Ra ratio of specific activities is 1.7. This is explained if we take into account the existence of ^{238}U in particulate, colloidal and dissolved phases in the Llobregat Basin, the presence of significantly higher concentrations of ^{238}U rather than ^{226}Ra in the dissolved and colloidal fraction (Camacho et al., 2010) and the physicochemical interactions between these phases. The observed disequilibrium could be explained by taking into account the fact that dissolved and colloidal ^{238}U enrich other colloids and particles in the LR basin with ^{238}U (Chabaux et al., 2008). Finally, most of these colloids and particles with an extra amount of ^{238}U are removed from the treated flow during coagulation, flocculation and particle settling, and are caught in the final sludge (Baeza et al., 2006; Gäfvert et al., 2002). On the other hand, direct precipitation of the dissolved ^{238}U as salt within the sludges is discarded as a significant enrichment pathway since the LR physicochemical properties (Table 1) are not favorable to this process (Baeza et al., 2006).

^{210}Pb is also not in secular equilibrium with its parent isotope, since it has two possible sources: ^{210}Pb coming from the ^{226}Ra present in the sludges, and ^{210}Pb coming from atmospheric deposition phenomena in the river basin, known as unsupported ^{210}Pb$_u$ (Grossi et al., 2016; Rose et al., 2013; Saari et al., 2010). The amount of ^{210}Pb$_u$ can be estimated as follows:

$$^{210}\text{Pb}_u\text{, specific activity=Total }^{210}\text{Pb, specific activity-}^{226}\text{Ra, specific activity} \quad (2)$$

Fig. 4 shows that there is a high correlation between $^{210}Pb_u$ (4-60 Bq·kg^{-1}) and ^{7}Be, a radionuclide of a cosmogenic origin. These results agree with those published in (Maringer, 1996) , which pointed out that ^{7}Be, ^{137}Cs and ^{210}Pb were transported in rivers bound to solids.

<u>^{232}Th decay chain</u>

In contrast to the behavior observed for the ^{238}U decay chain, similar median concentration values were obtained for ^{228}Ra and ^{228}Th (34and 37Bq·kg^{-1} and an interval of results of 28-44 and 27-43 Bq·kg^{-1} respectively) with a low RSD (11% and 12%, respectively). These results are different to the higher variabilities and ranges obtained in (Palomo et al., 2010a) for the short-lived ^{228}Ra and ^{228}Th decaying products, ^{228}Ac (12-212 Bq·kg^{-1}; RSD=37%) and ^{212}Pb (4-92 Bq·kg^{-1}; RSD=42%),respectively. The results near secular equilibrium, with a mean $^{228}Ra/^{228}Th$ ratio of 1.0 and low thorium solubility for the LR pH range (Table 1), indicated that both radionuclides would be mainly contained in the particles removed from the inflow water into the sludge.

<u>^{40}K, ^{7}Be and ^{137}Cs</u>

Natural ^{40}K showed the highest activity values (median value of 580 Bq·kg-1, range: 395-728 Bq·kg^{-1}; RSD=17%), followed by cosmogenic ^{7}Be (mean value of 82 Bq·kg^{-1}, range: 28-175 Bq·kg^{-1}; RSD=45%). However, artificial ^{137}Cs specific activity shows the lowest median activity value of the radionuclides quantified in sludges, 1.4 Bq·kg^{-1}, with a range of 1.0-2.7 Bq·kg^{-1} and a RSD of 32%.

The high ^{40}K activity values could be explained by the geological characteristics of the basin and the potassium NORM mining activity, and were similar to the wide ranges found in previous studies on DWTP sludges. However, the ^{40}K activities found in our study showed a significantly lower range than those found by Palomo et al. (2010a) (127-1321 Bq·kg^{-1}) at an Ebro River plant (Spain) and they were one order of magnitude lower than the maximum result of 4600 Bq·kg^{-1} reported in Palomo et al. (2010b) for a Guadalhorce River plant (Spain).

In the case of ^{7}Be, results are compatible with the wide range of results reported by other authors (4-353 Bq·kg^{-1}; (Fonollosa et al., 2014)). The high variability of the ^{7}Be content related to seasonal differences in the atmospheric wet and dry input fluxes in the LR basin area (Grossi et al., 2016) and sediment re-suspension phenomena (Saari et al., 2010).

As regards ^{137}Cs, the presence of this radionuclide in sludge is due to solids transported in rivers (Maringer, 1996). The ^{137}Cs activity values showed a lower range of 1.0-2.7 Bq·kg^{-1} than a previous study of an Ebro River treatment plant (0.9-6.5 Bq·kg^{-1} ;Palomo et al., 2010a)

<u>4.1.2. Sand</u>

The obtained results are detailed in Table 2. A slight increase in ^{228}Ra and ^{228}Th (^{232}Th series) activities can be observed in used sands. This result is possibly related to the progressive accumulation of particles and colloids at this treatment stage (Zevi et al., 2005). A large ^{40}K enrichment, one order of magnitude above the values observed in virgin sand, was observed. ^{40}K

enrichment is probably due to the same reasons as those predicted for ^{228}Ra and ^{228}Th. However, the higher accumulation is likely to be because of the biofilm that usually covers the sand grains (Haig et al., 2011), as it assimilates both nutrients and potassium, apart from the fact that ^{40}K is the most abundant radionuclide in the raw water flow (Montaña et al., 2013)(Table1).

In addition, ^{7}Be and ^{137}Cs could not be quantified above the minimum detectable activity (MDA), and no significant increase in the of ^{238}U decay chain isotopes was found.

4.1.3. GAC

Results for the activities found in GAC samples are given in Table 3 and showed as the mean ± standar deviation from the mean .

An increase in the activities of some isotopes belonging to the ^{238}U and the ^{232}Th decay chains can be observed, with a greater degree of enrichment for exhausted GAC, up to six times higher than the specific activities of virgin GAC. This phenomenon is more pronounced for ^{238}U with a maximum specific activity of 164±15 $Bq \cdot Kg^{-1}$ in exhausted carbons. In spite of the regeneration process, regenerated GAC showed a mean value of ^{238}U higher than virgin GAC which probably indicates that the pyrolysis process does not fully remove the ^{238}U, but reduces it significantly (mean relative reduction of 57% among exhausted and regenerated carbons). Furthermore, a slight but significant increase of ^{226}Ra, ^{228}Ra and ^{228}Th between virgin and exhausted GAC was verified.

The ^{210}Pb present in GAC may have two different origins, either the ^{210}Pb present in the water flow or the ^{210}Pb from the adsorbed ^{222}Rn (Watson and Crawford-Brown, 1991). As regards ^{40}K, in spite of its high content in raw water, no ^{40}K specific activity increase was found It is therefore possible to state that GAC did not retain dissolved ^{40}K. Results from the present study for GAC are similar to the values obtained in Australia (Kleinschmidt and Akber, 2008) for ^{226}Ra ^{210}Pb and ^{40}K. In the case of ^{238}U, the specific activity was one order of magnitude higher than the value obtained in the Australian study, which is possibly explained by the relatively low ^{238}U concentration in the Australian raw water (1.2 $mBq \cdot L^{-1}$; (Kleinschmidt and Akber, 2008)) in comparison with raw water from the LR (Table 1).

^{238}U/^{226}Ra (4.7±0.3),^{238}U/^{228}Ra (8.9±1.5) and ^{238}U/^{228}Th (8.9±0.6) mean ratios ± standard deviation in exhausted GACs are significantly higher than those found in sludges (1.7±0.4, 1.4±0.4 and 1.4±0.5). To explain this, the fact that GAC treats both LR water and groundwater should not be taken into account because treated groundwater represents a lower proportion of the total LR raw water processed (Table 1). In addition, as mentioned above, the aquifers are recharged mainly by LR infiltration and this would suggest that no significant differences are expected in the dissolved fraction of both waters. Therefore, the observed activity ratios are mainly due to the fact that river particles with lower ratios have been eliminated from the water flow in the particle settling step, and therefore very little ^{226}Ra, ^{228}Ra and ^{228}Th is present in the water flow at this stage. The observed ^{238}U activity values are related to the capacity of the GAC to remove ^{238}U through diffusion, pore transport and adsorption and can be estimated to be very low (<1%) due to the LR pH range (Kütahyalı and Eral, 2004; Mellah et al., 2006; Villalobos-Rodríguez et al., 2012).

Finally, the fact that the Iodine number is negatively correlated with the ^{238}U concentrations found in “regenerated”, “exhausted” and “in use” GACs should be highlighted (Fig. 5), confirming a progressive accumulation of these radionuclides, while the GAC adsorbs other compounds and becomes saturated.

4.1.4. RO brine

Results of the samples analyzed are shown in Table 2. ^{40}K was found in all of them, with a maximum value of 7±1 Bq·L^{-1}. This result follows previous research by our group, reported in (Montaña et al., 2013), which determined a removal capacity of 90% for beta activity in the RO step at the Llobregat DWTP by comparing the gross beta activities in raw and treated waters.

Although very significant reduction of alpha activity (mainly for uranium activity) was found (Montaña et al., 2013) for the RO step for the Llobregat DWTP, ^{238}U could not be quantified above the MDA in the studied samples since the estimated specific activity (~0,5 Bq·L^{-1}) was lower than the MDA of the applied methodology (gamma spectrometry, 4 Bq·L^{-1}).

4.2. Medically-derived ^{131}I

Results of ^{131}I activities in dry weight obtained for sludges, sands and GACs are shown in Fig. 6.The highest range of specific activities corresponded to dehydrated sludges, with relatively stable ^{131}I specific activity of 29-36 Bq·kg^{-1}. In contrast, atomized sludges showed a lower range of results <11-16 Bq·kg^{-1}. The ^{131}I relatively short half-life (8.02 days) together with the possibility of partial iodine vaporization (184°C) at the atomization process would explain the differences found between dehydrated and the final atomized sludges. ^{131}I was also found in sand samples with a maximum value of 6.1±0.5 Bq·kg^{-1}, but showed the lowest interval for specific activity compared with the other studied materials. As regards GAC samples, only 4 “in use” samples and 1 “exhausted” sample had quantifiable values with a maximum value of 28±8 Bq·kg^{-1}. No ^{131}I was found in the two RO brine samples analyzed (<1.0 and <1.4 Bq·L^{-1}).

The proposed distribution for medically-derived ^{131}I detailed in Hormann and Fischer (2015) for aquatic media is considered for discussion of the ^{131}I results: inorganic cation (^{131}I^{-}), dissolved organic and particulate. ^{131}I found in sludges was mainly associated with the ^{131}I contained in precipitated particles. The ^{131}I present in sands could be either due to the removal capacity of the sand for small particles or iodine that would be incorporated by the biofilm that usually covers sand grains. This biofilm adsorbs nutrients from the treated flow (Haig et al., 2011) and could intake dissolved organic iodine and I^{-}. Furthermore, as regards the ^{131}I found in GAC, it is possibly due mainly to the extremely high dissolved iodine adsorption efficiency of this material (Jeong et al., 2014; Park et al., 2015).

The presence of ^{131}I in sludge, sand and GAC could result directly from wastewater treatment plants discharges in the middle and low LR basin, upstream from the DWTP surface water catchment area. Biomedical ^{131}I removal by wastewater treatment plants is between 1-56% (Fischer et al., 2009; Ham et al., 2003; Punt et al., 2007).Therefore, ^{131}I is introduced into the physicochemical dynamics of the LR through plant discharges and is thus present in colloids, particles and is also quickly diagenetically remineralized (Rose et al., 2013).

4.3. Radiological risk assessment

A radiological evaluation of materials from the DWTP was done of waste and also for use in recycling and re-use (used and exhausted GACs, sand and sludge, dry weight). A specific evaluation for sludge recycling as a building material was carried out because of the good properties shown by atomized DWTP sludges for use in the concrete industry (Rodríguez et al., 2010).

Comparison of the obtained results with the corresponding exemption levels (Table 4)indicate that doses to individuals would be unlikely to exceed 1 mSv in a year.

As regards using sludge as a building material, the obtained gamma index (Table 4) showed that the 80% of the samples had I≤0.5, which means an external gamma dose of ≤0.3 mSv·y^{-1}, while the other 20% showed I values up to 0.54, which indicates that gamma dose would be well below 1 mSv·y^{-1} in all cases. Therefore, the gamma index is not expected to exceed the reference value in agreement with the radionuclide concentration variabilities obtained in the present study (Fig. 3).

Although ^{40}K content in reverse osmosis brine does not pose a radiological risk, it is possible to state that any discharge of this effluent into the Mediterranean Sea would not mean a significant increase of the existing natural concentration. ^{40}K values (Table 2) are lower than the activity of 12 Bq·L^{-1} corresponding to the potassium average in seawater (390 mg·L^{-1};Castro et al., 2007).

5. Conclusions

The present study provides information on the radioactivity content in by-products and different filtering materials from a large-scale Metropolitan DWTP treating both surface and groundwater. When possible, the results have been compared with the findings of other authors.

The distributions of radionuclides in by-products and different filtering materials from a DWTP, as well as the study of their correlations, have provided information on the different behavior of natural and artificial isotopes in the studied DWTP.

The highest specific activities (Bq·kg^{-1}; dry weight) reported for sludge (727±53), sand (766±37) and RO brine (7±2) correspond to ^{40}K .The maximum concentration in the case of exhausted GAC was found for ^{238}U (164±15) with lower mean values for regenerated and in-use GACs and significatively lower in virgin GAC confirming accumulation during its implementation. In addition, the measurements confirmed the presence of traces of biomedical ^{131}I (<1-38) in sludge, sand and GAC, which indicates its presence in raw water.

Furthermore, this work has provided information on the levels and variability of the activities of different radionuclides in sludge samples. Over a period of 6 years relative standard deviations (RSDs) ≤20% were found for ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, ^{40}K and ^{131}I. On the other hand, greater variability was observed (RSD ≥30%) for ^{238}U, ^{7}Be, ^{137}Cs and $^{210}Pb_u$.

The radiological risk of the analyzed materials was assessed by taking into account the exemption levels proposed by the European Commission and the IAEA. Although all these materials accumulated both natural and man-made biomedical radionuclides, they do not pose a radiological risk.

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Tables

Table 1. Raw water characteristics (2007-14).

	Min.	Median	Max.	SD	n
Llobregat River					
Flow treated per year ($m^3 \cdot s^{-1}$)	1.9	2.7	3.7	0.88	8
$HC0_3$ ($mg \cdot L^{-1}$)	174	402	581	71	88
Conductivity ($\mu S \cdot cm^{-1}$)	624	1493	3046	381	88
K ($mg \cdot L^{-1}$)	11	30	86	16	88
log [pH]	6.6	8.1	8.8	0.4	170
Suspended particles (2) ($mg \cdot L^{-1}$)	15	106	248	78	17
Gross Alpha Activity ($Bq \cdot kg^{-1}$)	500	800	1100	100	17
Gross Beta Activity ($Bq \cdot kg^{-1}$)	1200	1700	4400	100	17
Water (filtered <0.45µm)					
Gross Alpha ($Bq \cdot L^{-1}$)	0.031	0.064	0.12	0.017	45
Gross Beta ($Bq \cdot L^{-1}$)	0.447	0.83	1.482	0.229	45
Total Uranium ($Bq \cdot L^{-1}$)(1)	0.037	0.065	0.093	0.023	4
Cornellà Dwells					
Flow treated per year ($m^3 \cdot s^{-1}$)	0,24	0,61	1,15	0,32	8
Water (filtered <0.45µm)					
Gross Alpha ($Bq \cdot L^{-1}$)	0.053	0.091	0.145	0.022	21
Gross Beta ($Bq \cdot L^{-1}$)	0.735	1.032	1.217	0.148	21
K ($mg \cdot L^{-1}$)	24	34	40	5	20

(1) Data from 2003 to 2006 (A. Camacho et al. 2010)

(2) Data for particles >0.45 µm between 2012-14.

Table 2. Specific activities of ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, ^{7}Be, ^{40}K and ^{137}Cs determined in sands and RO Brine. Data below the detection limits is noted as <x.

	Bq·kg^{-1} (dry weight)							Bq·L^{-1}			
	Virgin sand (n=1)			Used sand (n=3)				RO brine (n=3)			
	Activity	±	Unc. (k=2)	Min.	-	Max.	n > MDA	Min.	-	Max.	n > MDA
^{238}U Series											
^{238}U	10	±	5	11	-	15	3			<4	-
^{226}Ra	9.6	±	0.7	8	-	10	3			<0.4	-
^{210}Pb	<10			<11	-	15	2			<6	-
^{232}Th Series											
^{228}Ra	5	±	1	5	-	12	3			<0.6	-
^{228}Th	6.3	±	0.5	7	-	14	3			<0.3	-
^{7}Be	<4.5					< 11	-			<2	-
^{40}K	12	±	5	20	-	766	3	5	-	7	3
^{137}Cs	<0.3					< 0.7	-			<0.2	-

Table 3. Iodine index(mg I_2 GAC g^{-1}) and specific activities of ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, ^{7}Be, ^{40}K and ^{137}Cs (Bq·Kg^{-1}) determined in virgin, regenerated, in-use and exhausted GACs

	Virgin (n=3)						Regenerated (n=5)						In-use (n=10)						Exhausted (n=4)					
	$\bar{x}$	±	S	Min.	-	Max.	$\bar{x}$	±	S	Min.	-	Max.	$\bar{x}$	±	S	Min.	-	Max.	$\bar{x}$	±	S	Min.	-	Max.
Iodine Index				N.D.	-	865	757	±	29	724	-	788	665	±	108	484	-	805	561	±	21	532	-	581
^{238}U Series																								
^{238}U						<24	63	±	9	53	-	73	86	±	21	60	-	121	148	±	14	129	-	164
^{226}Ra	7	±	3	4	-	10	11	±	2	9	-	13	13	±	7	4	-	29	32	±	3	29	-	34
^{210}Pb						<20						<15				<13	-	32	24	±	6	<19	-	31
^{232}Th Series																								
^{228}Ra	7	±	2	5	-	9	10	±	3	7	-	14	12	±	5	<4	-	22	17	±	4	12	-	22
^{228}Th	5	±	1	4	-	6	7	±	1	6	-	8	11	±	6	4	-	22	17	±	2	14	-	18
^{7}Be						<32						<57						<46						<20
^{40}K	39	±	2	<13	-	40						<18	46	±	19	<15	-	67	26	±	9	<15	-	34
^{137}Cs						<2						<1						<3						<1

<x=MDA

n=number of samples analyzed;

N.D.= No data

The results < MDA are not considered to quantify the $\bar{x}$ and S. MDA in the table equals the highest obtained.

Table 4. Ranges of the specific activities found above the MDA in solid materials (sludge, sand and GAC) and its corresponding exemption levels. Also the activity concentration index is shown and quantified in the sludges by applying the formula (1).

	Min.	-	Max.	Exemption level
Solid materials (Bq·kg^{-1})				
NORM radionuclies				
^{238}U series	4	-	164	<1000[a]
^{232}Th series	4	-	44	<1000[a]
^{40}K	15	-	766	<10000
Others				
^{7}Be	28	-	171	<10000
^{131}I	1	-	36	<10000
^{137}Cs	1	-	3	<100[a]
Sludge as a building material				
Index (I)	0.36	-	0.54	≤1

Exemption data from Euratom 2013/59 for any type of solid material

a: assuming secular equilibrium with its daughters

Figures

Fig 1. DWTP scheme and sampled by-products and materials (star). (UF=Ultrafiltration, RO=Reverse Osmosis, RM=Remineralization).

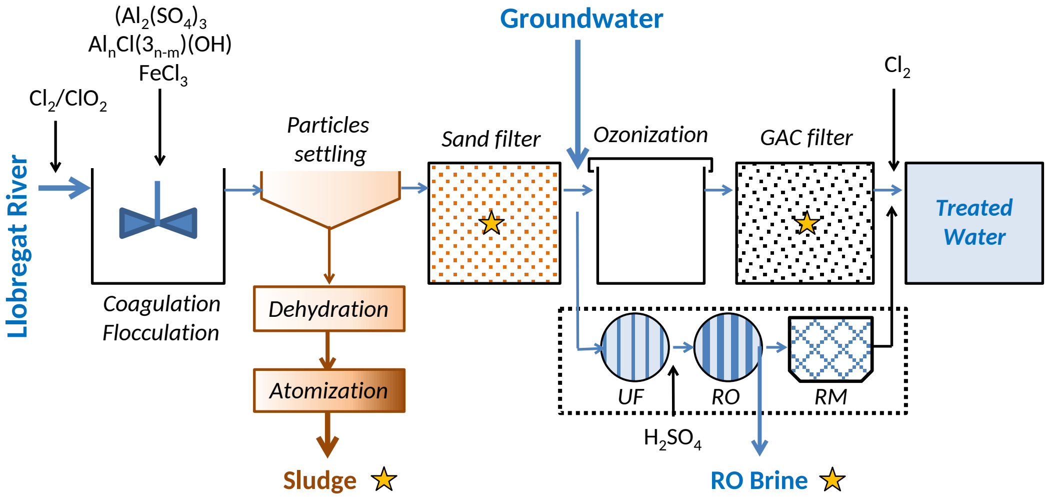
Fig. 2. GAC cycle in the DWTP. The sampled GACs are in bold.

Fig 3. Boxplot diagram with the radionuclides specific activities detected in 15 sludges (dry weight). ^{7}Be and ^{137}Cs shown one result below the MDA not included. Extreme cases (star) correspond to values lower than 1.5·Q1 or greater than 1.5·Q4.

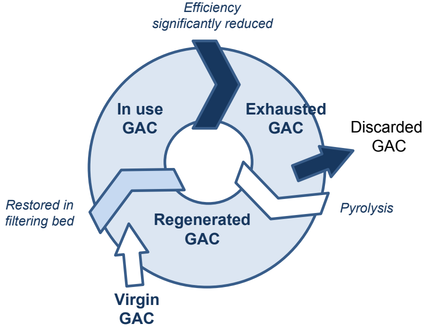
Fig. 4. Correlation determined in sludges between ^{7}Be and $^{210}Pb_u$. Data is represented with uncertainties (k=2) The correlation data correspond to linear regression and a line was drawn to follow it.

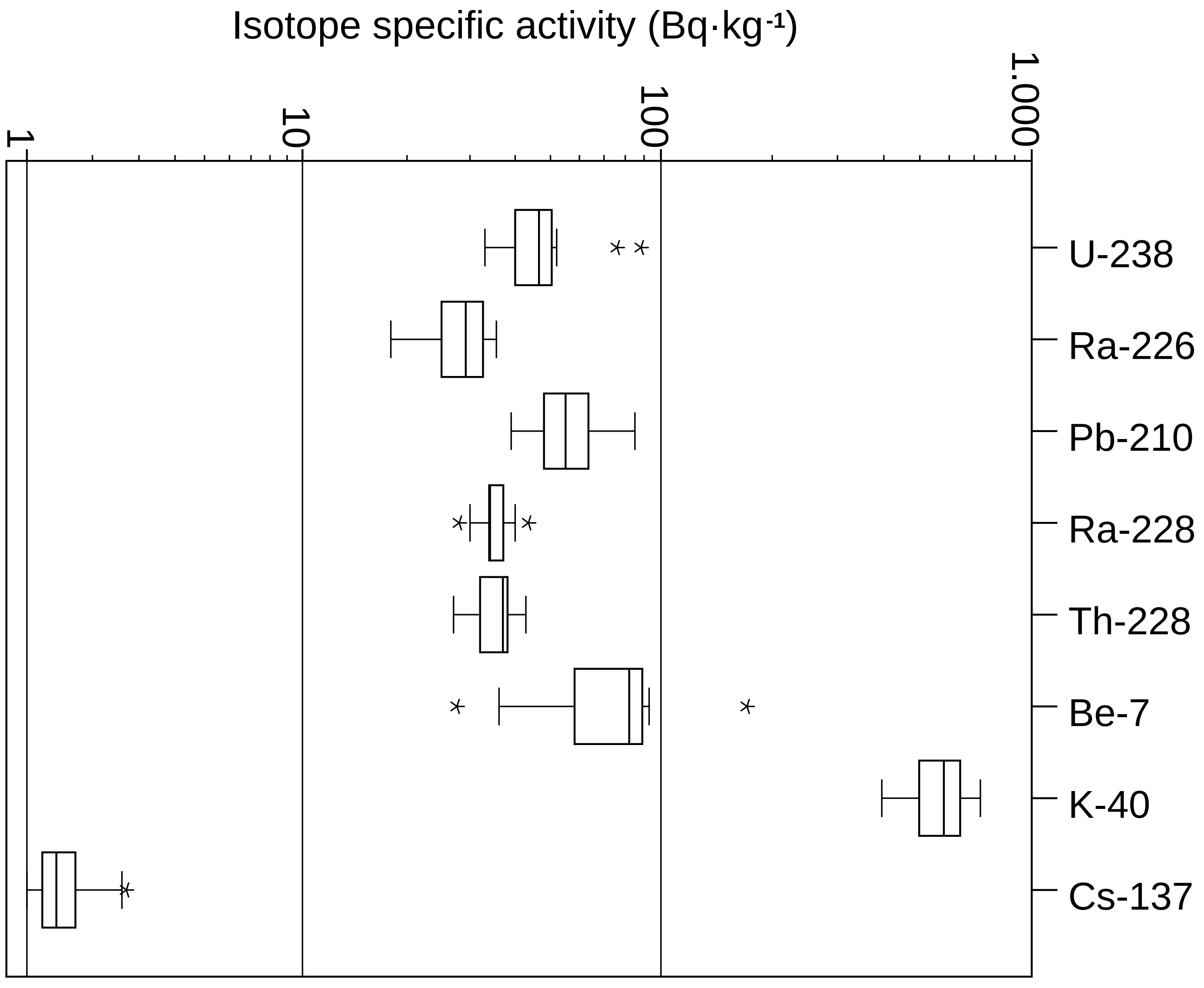
Fig. 5. Scatter plot between the Iodine Index and the ^{238}U specific activities with uncertainties (k=2) in regenerated, in use and exhausted GACs. Linear regression is suggested for the negative correlation.

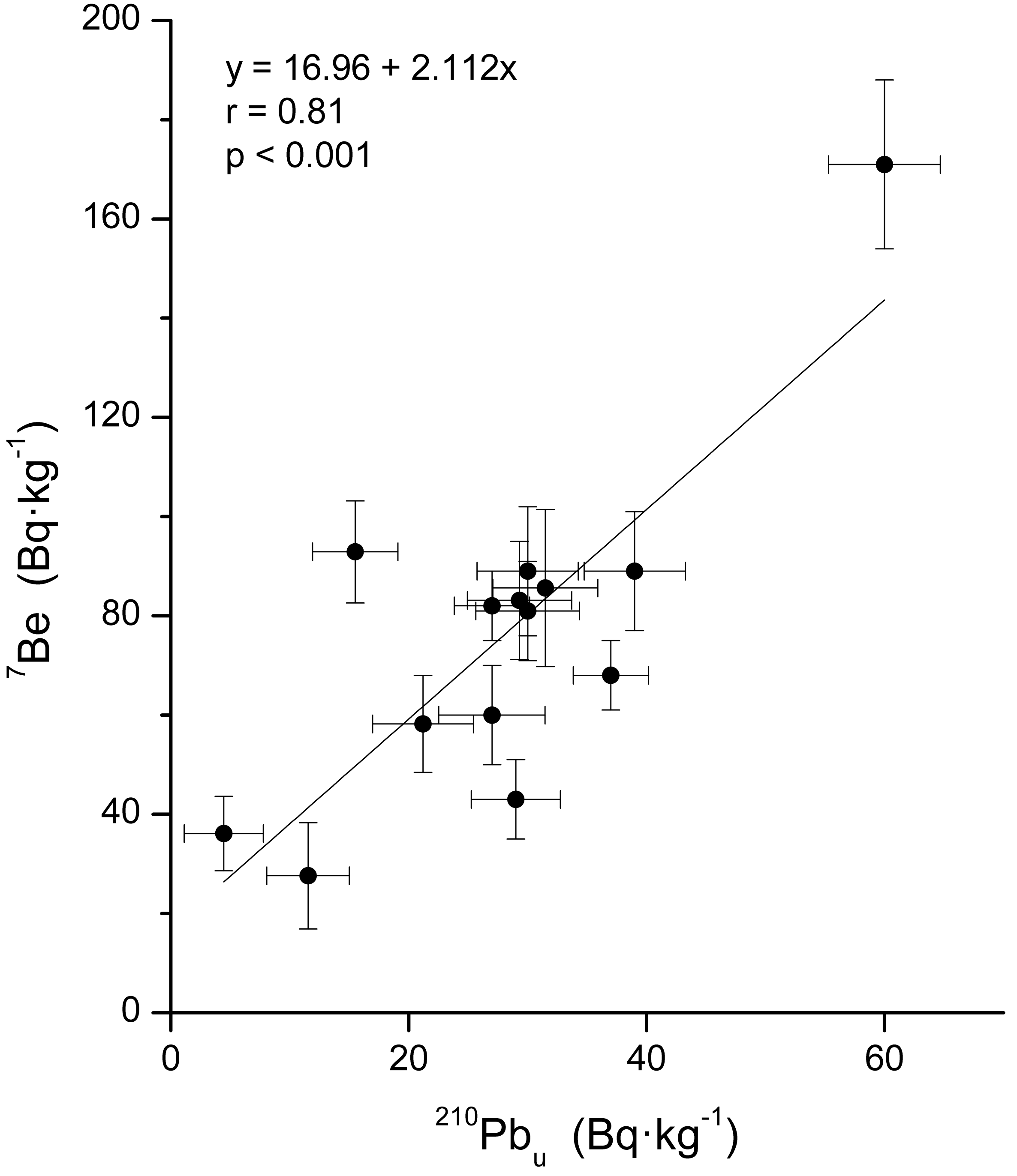
Fig. 6. ^{131}I specific activities (Bq·kg^{-1} in dry weight) with uncertainties (k=2) in dehydrated and atomized sludges, sand and in-use and exhausted GACs. Non-colored bars represent the MDA.

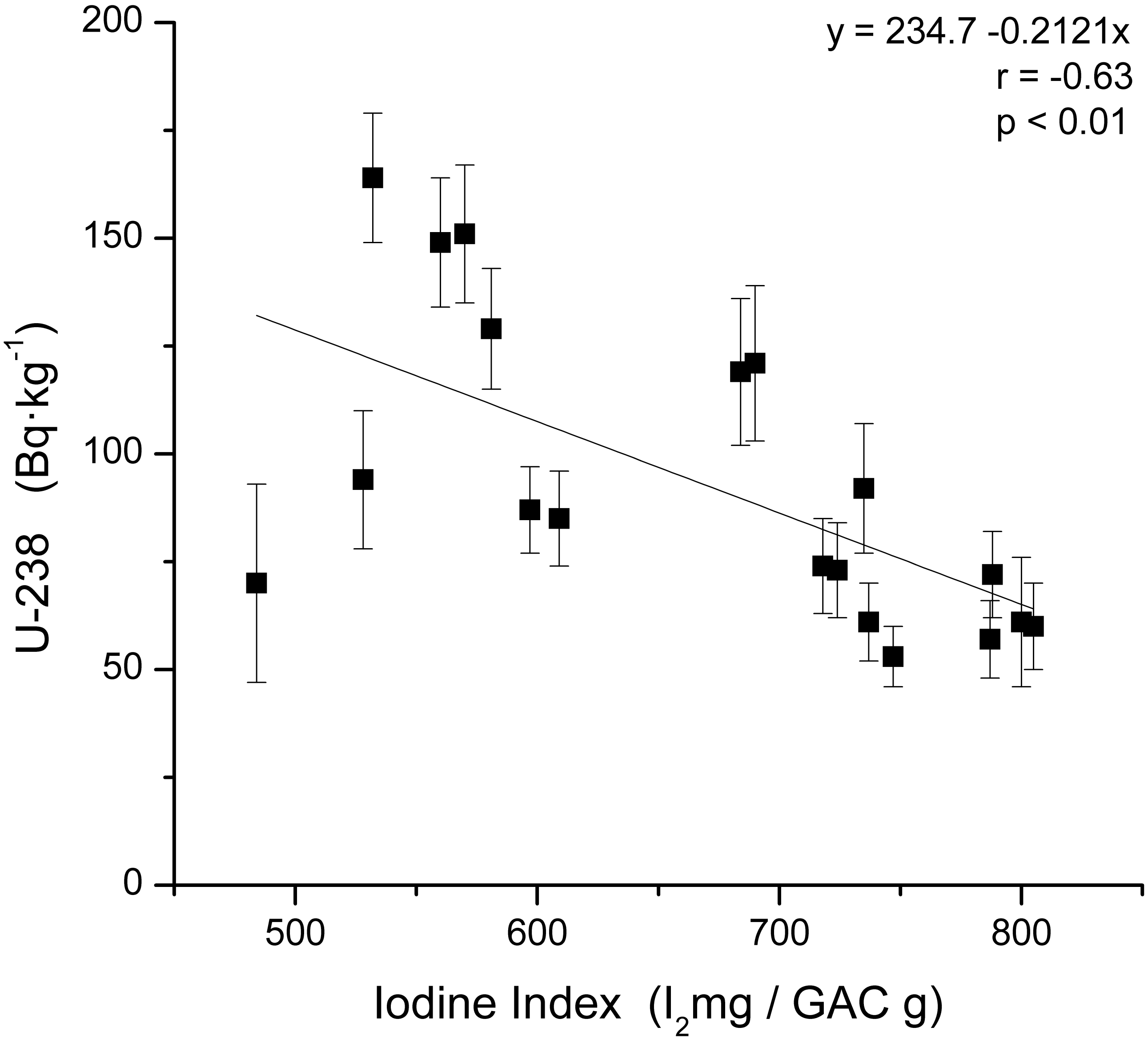


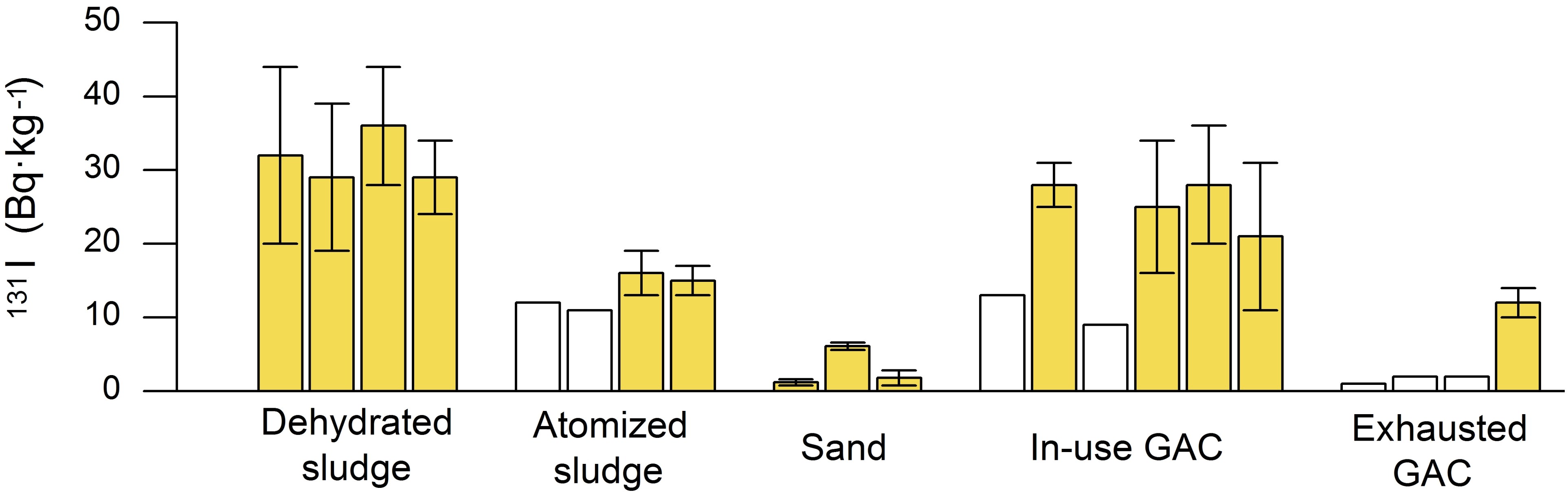
$(Al_2(SO_4)_3$
$Al_nCl(3_{n-m})(OH)$
$FeCl_3$
Cl_2/ClO_2
Llobregat River
Coagulation
Flocculation
Particles settling
Dehydration
Atomization
Sludge
Groundwater
Sand filter
Ozonization
GAC filter
Cl_2
Treated Water
UF
RO
RM
H_2SO_4
RO Brine


Efficiency
significantly reduced
In use
GAC
Exhausted
GAC
Discarded
GAC
Restored in
filtering bed
Pyrolysis
Regenerated
GAC
Virgin
GAC


Isotope specific activity (Bq·kg-1)
1
10
100
1.000
U-238
Ra-226
Pb-210
Ra-228
Th-228
Be-7
K-40
Cs-137


y = 16.96 + 2.112x
r = 0.81
p < 0.001
200
160
120
80
40
0
0
20
40
60
^{7}Be (Bq·kg^{-1})
^{210}Pb$_u$ (Bq·kg^{-1})


y = 234.7 -0.2121x
r = -0.63
p < 0.01
U-238 (Bq·kg^{-1})
200
150
100
50
0
500
600
700
800
Iodine Index (I_2mg / GAC g)


50
40
30
20
10
0
131 I (Bq·kg-1)
Dehydrated sludge
Atomized sludge
Sand
In-use GAC
Exhausted GAC