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SUIVI ET DEVENIR DES ORGANOETAINS DANS DES LIXIVIATS DE DECHARGE

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UNIVERSITY OF LJUBLJANA
FACULTY OF CHEMISTRY AND CHEMICAL TECHNOLOGY
AND
UNIVERSITY OF PAU AND PAYS DE L'ADOUR

RAZISKAVE USODE ORGANOKOSITROVIH SPOJIN V IZCEDNIH VODAH IZ DEPONIJ ODPADKOV

INVESTIGATIONS OF THE FATE OF ORGANOTIN COMPOUNDS IN LANDFILL LEACHATES

SUIVI ET DEVENIR DES ORGANOETAINS DANS DES LIXIVIATS DE DECHARGE

DOCTORAL DISSERTATION

Kelly Peeters

Ljubljana, April 2015

The submitted Doctoral Dissertation is a result of a 'cotutelle' study between the University of Ljubljana, Faculty of Chemistry and Chemical Technology and the University of Pau and Pays de l'Adour. The experimental work was done in the Department of Environmental Sciences of the Jožef Stefan Institute, Ljubljana, Slovenia and in the Laboratory of Analytical, Bio-Inorganic and Environmental Chemistry, LCABIE, UMR CNRS, IPREM, Pau, France.

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I hereby state that the submitted Doctoral Dissertation is a result of my autonomous research work.

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ABBREVIATIONS

BuLi	Butyl lithium
CH_3B_{12}	Methylcobalamin
CH_4	Methane
CO_2	Carbon dioxide
DBT	Dibutyltin
DMeT	Dimethyltin
DPhT	Diphenyltin
EC Directive	Directive of the European Parliament and of the Council
EDTA	Ethylenediaminetetraacetic acid
EQS	Environmental quality standard
Fe_3O_4NPs	Magnetite nanoparticles (mixture of FeO and Fe_2O_3 nanoparticles)
FeNPs	Iron nanoparticles
FeONPs	FeO nanoparticles
GC	Gas chromatography
HCl	Hydrogen chloride
H_2	Hydrogen
H_2O_2	Hydrogen peroxide
ICPMS	Inductive coupled plasma mass spectrometry
ID	Isotope dilution
IMO	International maritime organisation
MBT	Monobutyltin
MMeT	Monomethyltin
MSW	Municipal solid waste
$NaBEt_4$	Sodium tetraethylborate
NMR	Nuclear magnetic resonance
NPs	Nanoparticles

nZVI	Nano zerovalent iron
$OH^{\cdot}$	Hydroxyl radical
OTCs	Organotin compounds
PVC	Polyvinyl chloride
TBT	Tributyltin
TBTCl	Tributyltin chloride
TBTO	Tributyltin oxide
TeBT	Tetrabutyltin
TEM	Transmission electron microscopy
TeMeT	Tetramethyltin
TMAH	Tetramethyl ammonium hydroxide
TMeT	Trimethyltin
TPhT	Triphenyltin
TPrT	Tripropyltin
VFA	Volatile fatty acid
WHO	World Health Organisation

ABSTRACT

Organotin compounds (OTCs) are among the most toxic substances that were ever introduced into the environment by man. They are common pollutants in the marine ecosystems, but are also present in the terrestrial environment. Studies showed that detectable levels of OTCs can also be found in household products, which are disposed on landfills at the end of their life cycle. OTCs are then leached out of the wastes. Hence, landfill leachates can be considered as an important pool of OTCs.

In the investigations of the degradation and methylation processes of OTCs in environmental samples, the use of enriched isotopic tracers represents a powerful analytical tool. Sn-enriched OTCs are also necessary in the application of the isotope dilution (ID) mass spectrometry technique due to their accurate quantification. Since Sn-enriched monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) are not commercially available as single species, "in house" synthesis of the individual butyltin-enriched species is necessary. The preparation of the most toxic butyltin, namely TBT, was performed via a simple synthetic path, starting with bromination of metallic Sn, followed by butylation with butyl lithium. The formed tetrabutyltin (TeBT) was transformed to tributyltin chloride (TBTCl) using concentrated hydrochloric acid (HCl). The purity of the synthesised TBT was verified by speciation analysis using the techniques of gas chromatography coupled to inductively coupled plasma mass spectrometry (GC-ICPMS) and nuclear magnetic resonance (NMR). The results showed that TBT had a purity of more than 97 %. The remaining 3 % corresponded to DBT. The concentration of Sn in the synthesized ^{117}Sn-enriched TBT was determined by reverse ID-GC-ICPMS. The synthesis yield was around 60 %. The advantage of this procedure over those previously reported lies in its possibility to be applied on a micro-scale (starting with 10 mg of metallic Sn). This feature is of crucial importance, since enriched metallic Sn is extremely expensive. The procedure is simple and repeatable, and was successfully applied for the preparation of ^{117}Sn-enriched TBTCl from ^{117}Sn-enriched metal.

Since landfill leachates are an important pool of OTCs, transformation of OTCs in landfill leachate was investigated under simulated landfill conditions over a time span of six months. The degradation and biomethylation processes of OTCs were followed by the use of isotopically enriched tin tracers, namely ^{117}Sn-enriched TBT, ^{119}Sn-enriched DBT, ^{117}Sn-enriched $SnCl_2$, ^{117}Sn-enriched $SnCl_4$ and a ^{119}Sn-enriched butyltin mix containing TBT, DBT and MBT. Transformation of OTCs in spiked leachates was followed at *m/z* of the enriched

isotope of the enriched spikes and at *m/z* 120, which allowed simultaneous observation of the transformation of OTCs in the leachate itself and of the added spike. In parallel, these processes were also monitored in a non-spiked leachate sample at *m/z* 120. Quantification of OTCs was performed by GC-ICPMS. To discriminate between the biotic and abiotic transformations of OTCs and inorganic tin species, sterilization of the leachate was also performed and the data compared with non-sterilized samples. During the course of the experiment the microbial degradation of TBT was clearly manifested in Sn-enriched spiked leachate samples, while the abiotic pathway of degradation was observed for DBT. Biomethylation process was also observed in the leachate spiked with Sn-enriched Sn^{2+} or Sn^{4+}, in concentrations close to those found for total tin in landfill leachates. Monomethyl tin (MMeT) was formed first. Stepwise alkylation resulted in dimethyltin (DMeT) and trimethyl tin (TMeT) species formation. The hydrolysis of Sn^{2+} and Sn^{4+} species was found to be a limiting factor which controlled the extent of methyltin formation. The results of the present investigation importantly contribute to a better understanding of the processes that OTCs undergo in leachates, and provide useful information to managers of landfills for taking necessary measures to prevent the release of toxic methyltin species into the nearby environment.

The biotic and abiotic degradation of toxic OTCs in landfill leachates is usually not complete. Therefore, adsorption and degradation processes of TBT and TMeT in leachate samples treated with different iron nanoparticles (FeNPs): nanozerovalent iron (nZVI), iron oxide nanoparticles (FeONPs) and magnetite nanoparticles (Fe_3O_4NPs) were investigated to find conditions for their efficient removal. One sample aliquot was kept untreated (pH 8), while to the others (pH 8), FeNPs dispersed with tetramethyl ammonium hydroxide (TMAH) or by mixing were added. The samples were shaken under aerated conditions for 7 days. The same experiments were done in leachates in which the pH was adjusted to 3 with citric acid. The size distribution of TBT and TMeT between particles > 5000 nm, 450 - 5000 nm, 2.5 - 450 nm, and < 2.5 nm was determined by sequential filtration and their concentrations in a given fraction by GC-ICPMS. Results revealed that most of the TBT or TMeT were present in the fractions with particles > 2.5 or < 2.5 nm, respectively. At pH 8, the adsorption of TBT to FeNPs prevailed, while at pH 3, the Fenton reaction provoked degradation of TBT by hydroxyl radicals. TBT was the most effectively removed (96 %) when a sequential treatment of the leachate with nZVI (dispersed by mixing) was applied, first at pH 8, followed by a nZVI treatment of the aqueous phase, previously acidified to pH 3 with citric acid.

Such a treatment removed less effectively TMeT (about 40 %). It was proven that TMAH provoked methylation of ionic tin, so mixing was recommended for the dispersion of nZVI.

FeNPs are used for environmental water remediation. The NPs which persist in solution after the treatment may cause hazardous effects to the environment. To evaluate the potential environmental threat, the time dependent size distribution of iron particles was investigated in different aqueous samples after the FeNPs treatment. The efficiency of metal removal by FeNPs was also examined. Concentrations of metals in aqueous samples were determined, before and after the nanoremediation, by ICPMS. The data revealed that settling and removal of FeNPs after the treatment of environmental waters was related to the sample characteristics and the ways of NPs dispersion. The dispersion with TMAH was more effective than by mixing. When mixing was used for dispersion, nZVI, FeONPs and Fe_3O_4NPs were quickly settled in Milli Q water, forest spring water and in landfill leachate. The dispersion with TMAH resulted in a slower iron particles settling. In Milli Q and forest spring waters treated with FeONPs, a double layer of oleic acid and TMAH was formed around NPs, which prevented the formation of iron corrosion products. So, nanosized iron, which persisted in solution for at least 24 h after the treatment, represented a potential environmental threat. The removal of elements from environmental waters depended on the type of used FeNPs and the dispersion efficiency. The contaminant concentration and sample characteristics like the pH, the ionic strength, the content of organic matter, the presence of complexing ligands and the interactions of FeNPs with the sample matrix, as well as the chemical speciation of elements, contributed also considerably to the remediation efficiency. If the surface of FeNPs is contaminated by a particular metal, this contaminant may be during the NPs treatment released into the water, which is being remediated.

POVZETEK

Organokositrove spojine (OTCs) so med najbolj strupenimi substancami, ki jih je človek s svojimi dejavnostmi vnesel v okolje. OTCs se kot pogosta onesnažila pojavljajo v morskih ekosistemih, prisotne pa so tudi v kopenskem okolju. Najdemo jih v različnih gospodinjskih pripomočkih, ki jih po uporabi odložimo na odlagališča komunalnih odpadkov. Od tam se OTCs z atmosferskimi padavinami izpirajo iz odpadkov in se nabirajo v izcednih vodah.

Pri preučevanju procesov razgradnje in metilacije OTCs v okoljskih vzorcih, predstavlja uporaba obogatenih izotopov močno analizno orodje. Obogatene kositrove izotope OTCs uporabljamo tudi za točno kvantifikacijo OTCs z metodo izotopskega redčenja (ID) v masni spektrometriji. Ker obogateni izotopi monobutil kositra (MBT), dibutil kositra (DBT) in tributil kositra (TBT), kot posamezne zvrsti niso na voljo na tržišču, jih je potrebno sintetizirati v laboratoriju. Najbolj strupeno obliko OTCs, namreč TBT, smo sintetizirali po enostavnem postopku, začenši z brominiranjem kovinskega kositra, ki mu je sledila butilacija z butil litijem. Nastali tetrabutil kositer (TeBT) smo spremenili v tributil kositrov klorid (TBTCl) z uporabo koncentrirane klorovodikove kisline (HCl). Čistost sintetiziranega TBT smo preverili s speciacijsko analizo s tehniko plinske kromatografije v povezavi z masno spektrometrijo z induktivno sklopljeno plazmo (GC-ICPMS) in jedrske magnetne resonance (NMR). Rezultati so pokazali, da je čistost TBT večja od 97 %, DBT pa je bil prisoten le v 3 %. Koncentracijo kositra v ^{117}Sn-obogatenem TBT smo kvantificirali z metodo reverzne ID-GC-ICPMS. Izkoristek sinteze je bil okoli 60 %. Prednost postopka, pred predhodno objavljenimi v literaturi, je v možnosti, da sintezo izvedemo na mikro-nivoju (začenši s samo 10 mg kovinskega kositra). To dejstvo je izredno pomembno, saj so obogateni izotopi kovinskega kositra izjemno dragi. Postopek sinteze, ki smo ga razvili je enostaven, ponovljiv in omogoča pripravo ^{117}Sn-obogatenega TBTCl iz ^{117}Sn-obogatenega kovinskega kositra.

Ker so OTCs na komunalnih odlagališčih odpadkov prisotni v merljivih in okoljsko pomembnih koncentracijah, smo šest mesecev preučevali pretvorbe OTCs v izcednih vodah iz odlagališč. Razgradnji in biometilaciji OTCs smo sledili z uporabo izotopsko označenih sledilcev kositra, kot so ^{117}Sn-obogaten TBT, ^{119}Sn-obogaten DBT, ^{117}Sn-obogaten $SnCl_2$, ^{117}Sn-obogaten $SnCl_4$ in mešanice ^{119}Sn-obogatenih butilkositrovih spojin, ki je vsebovala TBT, DBT in MBT. Pretvorbe OTCs v izcedni vodi, ki smo ji dodali znano množino posameznih obogatenih izotopov kositra smo sledili na *m/z* obogatenega izotopa in na *m/z*

120, kar nam je omogočilo sočasno sledenje pretvorb OTCs v izcedni vodi, kakor tudi pretvorbam dodanih izotopsko obogatenih sledilcev kositrovih spojin. V vzporednem poskusu smo sledili tudi procesom pretvorb v vzorcu izcedne vode (ki ji nismo dodali sledilcev) na *m/z* 120. OTCs smo kvantificirali z GC-ICPMS. Da bi ločili med biotskimi in abiotskimi pretvorbami OTCs, smo alikvot izcedne vode sterilizirali in rezultate primerjali z nesteriliziranim vzorcem. Rezultati poskusov so pokazali, da je razgradnja TBT potekala z mikroorganizmi, medtem ko je razgradnja DBT potekala abiotsko. V vzorcih izcednih vod, ki smo jim dodali Sn-obogatene Sn^{2+} ali Sn^{4+}, smo potrdili proces biometilacije. Prvi se je tvoril monometil kositer (MMeT). V zaporednih korakih sta se nato tvorila dimetil kositer (DMeT) in trimetil kositer (TMeT). Omejitveni faktor pri tvorbi metil kositrovih spojin je hidroliza Sn^{2+} in Sn^{4+} zvrsti. Rezultati študije pomembno prispevajo k boljšemu razumevanju procesov pretvorb OTCs v izcednih vodah in so pomembni za upravljavce odlagališč odpadkov, ki lahko predvidijo ustrezne ukrepe za preprečitev izpusta strupenih metil kositrovih spojin v okolje.

Biotska in abiotska razgradnja OTCs v izcednih vodah iz odlagališč odpadkov mnogokrat ni popolna. Da bi našli načine učinkovite odstranitve TBT in TMeT iz izcednih vod, smo preučevali možnosti uporabe različnih nanodelcev železa (FeNPs): nano ničvalentno železo (nZVI), FeONPs in Fe_3O_4NPs. En alikvot vzorca izcedne vode smo obdržali neremediiran. Ta vzorec je imel pH 8. Drugim alikvotom vzorca pa smo pri pH 8 dodali FeNPs, ki smo jih dispergirali s tetrametil amonijevim hidroksidom (TMAH) ali z mešanjem vzorca. Vzorce smo nato stresali pod aerobnimi pogoji 7 dni. Enake eksperimente smo opravili v vzorcih izcednih vod, katerim smo pH nastavili na vrednost 3 s citronsko kislino. S sekvenčno filtracijo vzorca smo vzorec ločili na frakcije z velikostjo delcev > 5000 nm, 450 - 5000 nm, 2.5 - 450 nm in < 2.5 nm ter TBT in TMeT v ločenih frakcijah določili z GC-ICPMS. Rezultati so pokazali, da se je TBT nahajal pretežno v frakcijah z delci večjimi od 2.5 nm, TMeT pa je bil prisoten predvsem v raztopini, v frakciji z velikostjo delcev pod 2.5 nm. Pri pH 8 je prevladovala adsorpcija TBT na FeNPs, medtem ko se je pri pH 3, TBT razgradil s hidroksilnimi radikali, po mehanizmu Fentonske reakcije. TBT smo najbolj učinkovito odstranili (96 %) tako, da smo vzorcem zaporedoma dodali nZVI (dispergiran z mešanjem) pri pH 8, nato pa smo vodno fazo vzorca nakisali na pH 3 s citronsko kislino in vzorcu še enkrat dodali nZVI. Tak način remediacije z FeNPs je manj učinkovito odstranil TMeT (le okoli 40 %). Dokazali smo, da TMAH povzroči metilacijo ionskega kositra prisotnega v vzorcu, zato je za disperzijo nZVI potrebno uporabiti mešanje.

Kadar FeNPs uporabljamo za remediacijo vzorcev okoljskih vod, lahko NPs, ki ostanejo v vodni raztopini po končani remediaciji, onesnažijo okolje z nanodelci. Da bi ocenili, ali preostali nanodelci lahko predstavljajo nevarnost za okolje, smo v različnih časovnih razmikih sledili usedanju in velikostni porazdelitvi FeNPs v vzorcih okoljskih vod. Preučevali smo tudi učinkovitost odstranitve izbranih kovin z FeNPs. Koncentracije elementov v vzorcih vod pred in po nanoremediaciji smo določili z ICPMS. Rezultati so pokazali, da je usedanje delcev in s tem odstranitev FeNPs, iz vzorcev vod po remediaciji odvisna od karakteristik posameznega vzorca in načina disperzije. Disperzija nanodelcev s TMAH je bila bolj učinkovita kot z mešanjem. Ko smo za disperzijo nanodelecv uporabili mešanje, so se nZVI, FeONPs in Fe_3O_4NPs hitro usedali v Milli Q vodi, izvirski gozdni vodi in izcedni vodi iz odlagališč odpadkov. Pri disperziji s TMAH so se nanodelci usedali bolj počasi. V Milli Q in izvirski vodi, ki smo ji dodali FeONPs, se je okoli nanodelcev železa tvorila dvojna plast oleinske kisline in TMAH, ki je preprečila tvorbo železovih hidroksidov. Zato je nano železo, ki je ostalo v raztopini tudi še 24 h po remediaciji, predstavljalo nevarnost za okolje. Izkazalo se je, da je učinkovitost odstranitve elementov iz okoljskih vod odvisna od vrste FeNPs in učinkovitosti disperzije nanodelcev. K učinkovitosti remediacije so pomembno prispevali tudi koncentracija elementa v vzorcu, karakteristike vzorca kot so pH, ionska moč, vsebnost organske snovi, prisotnost ligandov, ki tvorijo komplekse s kovinami, interakcije FeNPs z matrico vzorca ter kemijska speciacija elementov. Če je površina FeNPs onesnažena z določeno kovino, se to onesnažilo lahko sprosti v vodo, ki jo remediiramo.

RESUME

Les organoétains sont parmi les substances les plus toxiques jamais introduites dans l'environnement par l'Homme. Ce sont des polluants communs dans les écosystèmes marins, qui sont également présents dans l'environnement terrestre. De nombreux types de déchets ménagers peuvent être à l'origine de la présence d'étain et plus particulier de ses composés organiques dans les centres de stockage de déchets (CSD). Les deux sources majeures peuvent être: les objets métalliques (cannettes, conserves…) pour l'étain minéral, et les formulations plastiques telles que le PVC, le silicone ou le polyuréthane (emballages, textiles…) qui contiennent des organoétains. Au cours de la dégradation des déchets, les composés de l'étain sont donc susceptibles d'être mobilisés dans les lixiviats et les biogaz.

Pour le suivi des procédures de dégradation et de méthylation des organoétains dans les échantillons environnementaux, l'utilisation de traceurs isotopiques enrichis représente un outil d'analyse puissant. Les organoétains enrichis sont également nécessaires lorsque la spectrométrie de masse avec dilution isotopique est utilisée pour la quantification précise des organoétains. Parce que le monobutylétain (MBT), le dibutylétain (DBT) et le tributylétain (TBT) isotopiquement enrichis en étain ne sont pas disponibles individuellement, leur synthèse est nécessaire. La préparation du butylétain le plus toxique, le TBT, a été réalisée par bromation de Sn métallique, puis par butylation avec du butyl-lithium. Le tétrabutylétain (TeBT) formé, a été transformé en chlorure de tributylétain (TBTCl) en utilisant de l'acide chlorhydrique concentré (HCl). La pureté du TBT synthétisé a été vérifiée par analyse de spéciation utilisant la chromatographie en phase gazeuse couplée à un spectromètre de masse à plasma induit (GC-ICPMS) et la résonance magnétique nucléaire (RMN). Les résultats ont montré que le TBT avait une pureté de plus de 97 %, les 3 % restants correspondant à du DBT. Les organoétains ont été quantifiés par dilution isotopique inverse par GC-ICPMS. Le rendement de la synthèse est d'environ 60%. L'avantage de cette procédure est la possibilité d'être appliquée sur une micro-échelle (à partir de 10 mg de Sn métallique). Ceci est d'une importance cruciale, car l'étain métallique enrichi est extrêmement coûteux. La procédure est simple et reproductible et elle a été appliquée avec succès à la préparation du TBTCl enrichi en ^{117}Sn à partir du métal enrichi en ^{117}Sn.

Parce que les lixiviats de décharge contiennent des organoétains, leur transformation dans ces lixiviats a été étudiée dans des conditions simulées pendant six mois. La dégradation et la méthylation ont été suivies par l'utilisation de traceurs d'étain avec des isotopes enrichis, à savoir TBT enrichi en ^{117}Sn, DBT enrichi en ^{119}Sn, $SnCl_2$ enrichi en ^{117}Sn, $SnCl_4$ enrichi en

^{117}Sn et un mélange de butylétains enrichi en ^{119}Sn et contenant TBT, DBT et MBT. Les transformations dans les lixiviats de décharge ont été suivies à *m/z* de l' isotope enrichi des étalons enrichis et à *m/z* 120. Ceci a permis l'observation simultanée de la transformation des organoétains dans le lixiviat et de l'effet de l'étalon ajouté. En parallèle, ces procédures ont également été utilisées dans un échantillon de lixiviat sans étalon à *m/z* 120. La quantification des organoétains a été réalisée par GC-ICPMS. Pour discriminer les transformations biotiques des transformations abiotiques, des organoétains et étain inorganique, la stérilisation des lixiviats a également été réalisée et les données comparées avec celles obtenues pour les échantillons non-stérilisés. Au cours de l'expérimentation, la dégradation microbienne du TBT a été clairement observée dans le lixiviat dans lequel du TBT enrichi avait été ajouté. En revanche, la dégradation observée pour le DBT est abiotique. Un phénomène de biométhylation continu a également été observé dans le lixiviat dans lequel avait été ajouté Sn^{2+} ou Sn^{4+} enrichi en Sn, conduisant à la formation du monométhylétain (MMeT), puis, par alkylations successives, au diméthylétain (DMeT) et au triméthylétain (TMeT). L'hydrolyse de Sn^{2+} et Sn^{4+} est un facteur limitant qui contrôle le degré de formation des méthylétains. Les résultats de cette étude sont une contribution à une meilleure compréhension des processus de transformation et de dégradation des organoétains dans les lixiviats ; ils représentent également des informations utiles pour les mandataires de CSD afin de prendre les mesures nécessaires pour prévenir la libération de méthylétains toxiques dans l'environnement.

L'appréhension des processus de transformation biotique et abiotique des organoétains dans les lixiviats de décharge a été complétée par l'étude de l'adsorption et de la dégradation du TBT et du TMeT dans des échantillons de lixiviat traités avec différentes nanoparticules de fer (FeNPs): fer nano-valent (nZVI), FeONPs et Fe_3O_4NPs ont été considérés afin de trouver des conditions efficaces d'élimination de ces deux composés. Différents aliquotes d'échantillon de lixiviat ont été traités à pH 8 avec des FeNPs dispersées avec de l'hydroxyde de tétraméthyl ammonium (TMAH) ou par agitation. Les échantillons ont été agités dans des conditions aérées pendant 7 jours. Des expérimentations similaires ont été réalisées avec des aliquotes de lixiviats dans lesquels le pH avait été ajusté à 3 avec de l'acide citrique. La distribution de TBT et TMeT entre les particules avec une taille > 5000 nm, 450 - 5000 nm, 2.5 - 450 nm et < 2.5 nm a été déterminée par filtration séquentielle. Leurs concentrations dans chacune des fractions en taille ont été déterminées par GC-ICPMS. Les résultats ont révélé que la majorité du TBT est présente dans les fractions avec des particules > 2.5 nm, alors que le TMeT est essentiellement dans la fraction < 2.5 nm. A pH 8 l'adsorption du TBT par FeNPs domine, tandis qu'à pH 3, la réaction de Fenton provoque la dégradation du TBT par les radicaux hydroxyles. Le TBT est plus efficacement éliminé (96%) lorsque un traitement séquentiel des lixiviats avec nZVI (dispersé par agitation) est appliqué, d'abord par mise en contact à pH 8, puis par traitement de la phase aqueuse avec nZVI acidifiée à pH 3 avec de l'acide citrique. Ce traitement s'est avéré moins efficace pour le TMeT, éliminé seulement à environ 40%). De plus, il a été démontré que le TMAH provoque la méthylation de l'étain. Par conséquent, il est recommandé d'utiliser une agitation plutôt que le TMAH pour disperser nZVI.

Lorsque les FeNPs sont utilisées pour le traitement de l'eau, les nanoparticules qui persistent dans le milieu après le traitement peuvent avoir un impact néfaste pour l'environnement. Pour en évaluer le risque potentiel, les nanoparticules de fer ont été suivies dans différents échantillons aqueux après traitement par FeNPs. En particulier leur distribution en taille a été déterminée en fonction du temps. L'efficacité d'élimination des métaux par FeNPs a aussi été examinée, les concentrations de métaux dans des échantillons aqueux étant déterminées avant et après nano-assainissement, par ICPMS. Les données ont révélé que la précipitation des nanoparticules après traitement des eaux environnementales par des FeNPs dépend des caractéristiques des nanoparticules utilisées et de leur mode de dispersion. Ainsi la dispersion par le TMAH est plus efficace en comparaison de la dispersion par agitation. Dans ce dernier cas, nZVI, FeONPs et Fe_3O_4NPs précipitent rapidement lorsqu'ils sont en suspension de l'eau Milli Q, dans une eau de source (forêt) et dans les lixiviats de décharge. La dispersion avec le TMAH induit une sédimentation plus lente des particules de fer. Dans l'eau Milli Q et l'eau de source traitées avec FeONPs, la formation probable d'une double couche d'acide oléique et de TMAH autour des nanoparticules, empêche la formation de produits de corrosion du fer. Ainsi, le fer nanométrique persistant dans la phase aqueuse encore 24 h après le traitement, représente une menace potentielle pour l'environnement. L'élimination des éléments présents dans les eaux environnementales est apparue dépendre du type de FeNPs et l'efficacité de la dispersion. La concentration de ces éléments et les caractéristiques de ces eaux comme le pH, la force ionique, la quantité de matière organique, la présence de ligands complexants, les interactions des FeNPs avec les composants de la matrice, ainsi que la spéciation chimique des éléments, contribuent considérablement à l'efficacité du traitement. De plus, si un métal particulier s'avère être sorbé à la surface des nanoparticules de fer, ce métal peut être libéré dans l'eau au cours de son traitement avec les nanoparticules, venant alors ainsi la (re)contaminer.

1 INTRODUCTION

1.1 ORGANOTIN COMPOUNDS

Organotin compounds (OTCs) are substances that are characterised by the presence of one or more covalent bonds between atoms of carbon and tin. They have the general formula R_nSnX_{4-n} (n= 1-4), where R is an alkyl or aryl group, while X is an anionic species (for example chloride, oxide, hydroxide or a group attached to tin through oxygen, sulphur, nitrogen, halogen, etc. (Blunden and Evans, 1990; de Carvalho Oliveira and Santelli, 2010; Rüdel, 2003; Ebdon et al., 1998; Rosenberg, 2005).

Credit for the first systematic study of OTCs belongs to Sir Edward Frankland, who in 1852 described his initial results on the preparation of ethyltin compounds (Seyferth, 2001). These OTCs remained no more than laboratory curiosities for nearly 100 years since they did not reveal any obvious commercial potential. This changed in the 1940s when the plastic industry began to expand. Their biocidal properties were discovered in the late 1950s (de Carvalho Oliveira and Santelli, 2010; Rosenberg, 2005; Hoch, 2001).

Today, tin has a larger number of its organometallic derivatives in commercial use than any other element. This is because OTCs are remarkably various in their physical, chemical and biological properties.This is reflected in divergent OTCs industrial applications (Hoch, 2001). The majority of the organotin uses are comprised of five major commercial applications: polyvinyl chloride (PVC) heat stabilizers, biocides, catalysts, agrochemicals and glass coatings (Batt, 2006). The various commercial applications gave rise to a drastic increase in the worldwide production of organotin chemicals (de Carvalho Oliveira and Santelli, 2010; Rosenberg, 2005; Hoch, 2001).

1.1.1 Industrial applications and the source of environmental pollution

<u>PVC stabilizers:</u> In the 1940s, the value of the PVC polymer began to be realised. This polymer suffered from the disadvantages that, under the effects of heat or light, it degraded

with a consequent embrittlement and discolouration. A search was made for a compound, which would inhibit this degradation. That is how the powerful stabilising action of certain OTCs derivatives was revealed. A breakthrough in their use occurred in 1955 when a government approval was obtained for the use of non-toxic octyltin stabilisers in PVC, intended for food-contact applications, for example in PVC bottles for fruit squashes or vegetable oils. The stabilisation of PVC has remained the largest application of OTCs up until the present day (Blunden and Evans, 1990).

Antifouling paints: Since the first days of sailing, mariners have been battling ‘fouling’ – the growth of barnacles, seaweeds, tubeworms, and other organisms on boat bottoms. Fouling produces roughness on the surface of the bottom of the vessel, thereby increasing the turbulent flow and drag. This causes also the extra disadvantage of an increase in fuel consumption of about 0.3-1.0 %. The Phoenicians already realised that smoother bottoms translated into easier rowing and faster sailing and were the first to nail copper strips on the hulls of their ships to inhibit fouling. In naval actions, the cleaner, faster vessel often escaped stronger forces or caught up with slower ones. Although copper strips have been replaced by advanced high-technological antifouling coatings, fouling remains more important today than ever to both naval and commercial fleets. Fouling affects all vessels, from supertankers to fishing and sailing boats (Champ and Seligman, 1996).

OTCs are one of the most effective classes of biocides utilized against fouling. A widespread use of tributyltin (TBT)-based antifouling paints began in the early 1970s. An antifouling paint consists of a film-forming material with a biocidal ingredient and a pigment. It works by releasing small amount of the biocide from the painted hull into the water, forming a thin envelope of highly concentrated TBT around the boat (Hoch, 2001).

Surfaces treated with modern TBT-based copolymer paints are designed to reach a constant TBT leach rate of 1.6 μg Sn cm^{-2} per day. The leaching rate of freshly painted surfaces will be even as high as 6 mg Sn cm^{-2} per day, and is reduced in several weeks to the desired constant rate. For example, during a 3-day stay in a harbour, a commercial ship, leaching TBT at a constant leaching rate, can release more than 200 g of TBT into the water. If freshly painted, this amount can reach even 600 g. Despite the fact that TBT is sparingly soluble in water, the dissolved fraction may contribute to severe contamination of the surrounded water, where the TBT concentration can reach up to 200 or 600 ng Sn L^{-1}, respectively. So, it is no surprise to find the major sites of TBT pollution in harbours with large commercial vessels and near docks or other facilities where shipbuilding, repairing and repainting occurs. TBT, the active ingredient in antifouling paints, may be the most acutely toxic chemical to some sensitive aquatic organisms, ever deliberately introduced into the aquatic environment (Hoch, 2001; Cima et al., 2003).

Catalysts: Catalysts are used to speed up chemical reactions, especially during polymerization. The most common applications for mono-and diorganotin catalysts are in chemical synthesis and the curing of coatings.

In chemical synthesis, the OTCs are used for the esterification and transesterification of mono- and polyesters. These products are then used for plasticizers, synthetic lubricant manufacturing, and polyester polyol production, as well as some coating applications.

As curing catalysts, one of the largest uses of OTCs is in electro-coatings. These products are sold into a wide range of applications, with the largest being automotive, where they provide excellent rust resistance. The catalysts are also used in urethane coatings as well as in the polyurethane foam production. Other applications include curing silicones and silanes (Batt, 2006).

Glass coatings: Monoorganotins, mainly monobutyltin (MBT) trichloride are used on glass containers in Hot End Coatings. It is deposited on the hot glass surface of bottles thereby preventing micro-fractures.

On flat glass, mono- and diorganotins, deposited by chemical vapour deposition, are used in the manufacture of low thermal emissivity glass. They reduce the heat loss through the coating deposited on the glass surface (Batt, 2006).

Agriculture: Since the early 1960s both triphenyltin (TPhT) hydroxide and TPhT acetate have been used to control fungal diseases causing leaf spot on sugar beets, celery, carrots, onions and rice, and are also used to prevent tropical plant diseases in peanuts, pecans, coffee and cocoa. These non-systemic fungicides show excellent sticking properties, rain fastness and a good persistence on the plant surface.

Although the toxic effects of OTCs against various organisms are well known, these compounds are still applied in the agriculture, eventhough with certain restrictions. Nevertheless, the World Health Organization (WHO) pronounced TPhT compounds as ‘safe agricultural chemicals’ because their concentrations on treated plants decrease rapidly due to the influence of light, losses in wind and rain and degradation in the atmosphere (Hoch, 2001).

Timber treatment: Wood is attacked by insects, fungi and bacteria. This results in the breakdown of the cellulose and other complex substances. To prevent wood degradation, timbers are treated with TBT. After evaporation of the solvent the pollutants remain safely within the wood structure, due to their low vapour pressures. Also TBT leaching from the wood is considered to be negligible (Hoch, 2001).

1.1.2 Appearance of organotin compounds in the environment

Since OTCs find such a wide variety of industrial applications, there are, consequently, a large number of pathways which can be envisaged for their entry into the environment.

The possible routes by which OTCs enter the environment are: (a) leaching/weathering, (b) land burial and (c) incineration of waste material. Of these, atmospheric release of OTCs by incineration is probably not significant, as they undergo thermal decomposition to inorganic tin compounds at combustion temperatures.

Although the biocidal uses of organotin chemicals comprise only approximately 30 % of the total world consumption, they probably give rise to the largest proportion of free OTCs in the environment, due to their direct introduction into natural media. Because of the manner in which biocides are applied (often aerial spraying), there is the possibility that not only the soil, but also the air and adjacent waterways, could be contaminated. After spray application, biocides will be removed by adsorption onto the soil before they can enter surface waters.

Direct entry of OTCs into the aqueous environment is primarily due to their use in antifouling paint systems (Blunden et al, 1984).

1.1.3 Fate of organotin compounds in the environment

The persistence of OTCs in polluted ecosystems is a function of physical (e.g. adsorption to suspended solids and sediments), chemical (e.g. chemical and photochemical degradation) and biological (e.g. uptake and biological degradation) mechanisms. Thus, it is important to study the distribution and the transformation processes of these pollutants under natural conditions.

1.1.3.1 Degradation of organotin compounds

The degradation of an OTC may be defined as the progressive removal of the organic groups from the tin atom by breaking of the Sn-C bound. This stepwise loss of organic groups from the tin atom is accompanied by a progressive lowering in biological activity.

$R_4Sn \rightarrow R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4$

Degradation can occur by a number of different processes. These include: (a) UV irradiation, (b) biological cleavage, (c) chemical cleavage, (d) γ-irradiation and (e) thermal cleavage. Only processes (a), (b) and (c) are considered in the environment because γ-irradiation has a negligible intensity at the earth's surface and thermal cleavage is also unlikely to be of environmental significance, because the Sn-C bond is reported to be stable at temperatures up to 200°C (Hoch, 2001,Baig et al., 1996; Chiemchaisri et al., 2004).

UV irradiation: The light emitted by the sun, reaching the earth's surface, consists mostly of wavelengths above 290 nm. UV light with a wavelength of 290 nm possesses energy of approximately 300 kJ mol^{-1}, while the mean bound dissociation energies for some Sn-C bounds are found to be in the range of 190 - 220 kJ mol^{-1}. Therefore, as the maximum absorption wavelength of OTCs is generally within the UV region, Sn-C bound cleavage could occur.

Photolysis by sunlight appears to be the fastest route of degradation in water. But because of the attenuation of sunlight with the depth in the water, photolysis is probably not important at greater depths, or in sediments and soils (Hoch, 2001; Blunden et al., 1984; Rosenberg, 2005).

Biological cleavage: Studies showed the degradation of OTCs in soils without the presence of light. Since carbon dioxide (CO_2) was evolved and the breakdown did not occur in sterile soil, it was concluded that the degradation was due to the ability of certain microorganisms to metabolise the OTCs. Degradation occurs faster under aerobic than anaerobic conditions. However, the biological activity is restricted by the toxic concentrations of OTCs and other limiting conditions concerning the life of the microorganisms like light, temperature or nutrients (Hoch et al., 2001; Blunden et al., 1984; Rosenberg, 2005).

Chemical cleavage: There are are two important reaction types that result in a Sn-C bound cleavage.

The Sn-C bound is capable of polarization in either direction and is therefore susceptible to attack by both nucleophilic and electrophilic reagents. Compounds that can react with OTCs are mineral acids, carboxylic acid, alkalimetals, etc. Also free radical processes can cause hemolytic Sn-C bound fission because the Sn-C bound is a fairly good radical trap (Hoch et al., 2001; Blunden et al., 1984; Rosenberg et al., 2005).

1.1.3.2 Biomethylation

Methylated tin is more toxic than inorganic tin, so methylating activities in the environment can have profound potential implications for both the human health and the environment (Björn et al., 2011). In addition to anthropogenic sources of methyltin emission, they may also be produced by biomethylation of Sn(II) and/or Sn(IV).

Methylcobalamin (CH_3B_{12}) has been shown to methylate a wide range of metals and metalloids and it is the only naturally occurring methylating agent, which is capable of transferring the methyl group as a carbanion. Under suitable conditions it is also capable of transferring a methyl group as a free radical or as a carbonium ion (Ashby and Craig, 1988). The methylation of Sn (see Figure 1) requires the presence of oxygen for the generation of radical species. A stannyl radical ($Sn(III)^\bullet$), is formed via the reduction of Sn(IV) or due to the presence of a single-electron oxidant such as Fe(III) or Co(III), which oxidizes Sn(II). The $Sn(III)^\bullet$ then reacts with CH_3B_{12}. Homolytic cleavage of CH_3B_{12} by $Sn(III)^\bullet$ gives MMeT (Ridley et al., 1977).

The transfer of the first methyl group to an inorganic metal atom is the most important step in the formation of organometalic species in the environment. Di-, tri- and tetramethyl species may then be formed by a stepwise methylation (Ashby and Craig, 1988; Thayer, 2002).

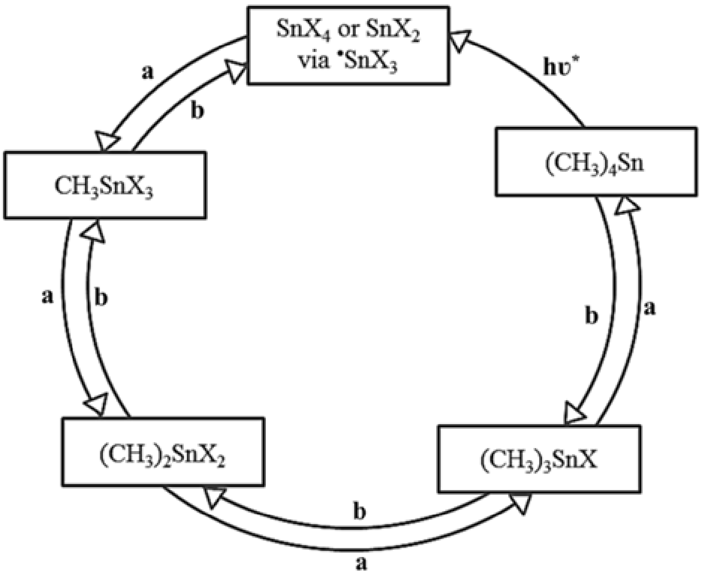

Figure 1: Subsequent methylation processes of ionic tin to form organomethyltins. Adapted from ref. Ridley et al., 1977.

Laboratory studies showed that also biomethylation of butyltin species can occur. In this way metylbutylspecies are formed, with methyltributyltin being the most abundant (Hoch et al., 2001; Rosenberg, 2005).

1.1.4 Toxicity of organotin compounds

The toxicological properties of OTCs follow a very complex pattern, but in general the biological effects of OTCs are mostly dependent on the number of organic groups bound to the central Sn atom. The toxicity of anions does not play a significant role and is important only in the case when the anion is toxic itself. In such a case, the biological effects of the cation and anion are cumulative. The increase in the chain length of the alkyl moiety is accompanied by a stronger decrease of its biocidal activity, making long chain species such as the octyltin compounds basically nontoxic for mammals. So, these compounds are considered safe to use as stabilizers in PVC materials or in food packaging. There is a maximum biological activity for triorganotin compounds (R_3SnX). Within any R_3SnX series, species specificity is markedly dependent upon the nature of the organic groups (Table 1) (Rosenberg, 2005; Hoch, 2001; World Health Organization, 1990).

Table 1: Living organisms, which are the most influenced by certain trisubstituted organotin derivatives. Adapted from ref. Hoch, 2001.

Species	**R in R_3SnX compound**
Insects	Me
Mammals	Et
Bacteria	Pr
Bacteria, fish, fungi, molluscs, plants	Bu
Fish, fungi, molluscs	Ph
Fish, mites	Cyclo-C_6H_{11}, $PhMe_2CCH_2$

Organotin lipophilicity plays a key role in both, the bioaccumulation and the mechanism of action, since the potential toxicity depends on their high affinity for cell membranes. Their ability to cross biological membranes permits them to penetrate easily into cells and their organelles and to interact with several intracellular targets (Okoro et al., 2011).

The underlying cause of the broad spectrum of acute toxicity shown by triorganotin compounds is due to the derangement of mitochondrial functions (Blunden et al., 1984):

- The interaction of OTCs with mitochondrial membranes causes swelling and disruption.
- OTCs are able to react as ionophores which derange mitochondrial functions through intervention in the Cl^-/OH^- exchange across the lipid membrane.
- The main mechanism of all OTCs is their ability to inhibit mitochondrial oxidative phosphorylation by inhibiting the fundamental energy processes of the cell system.

1.1.4.1 Effects on aquatic species

TBT, which was introduced into the marine environment via antifouling paints, is highly toxic to marine organisms.

It causes shell deformations of growing oysters and a high mortality of the larval state of oysters and other bivalves. In addition to shell malformations, poor growth and reduction in the tissues was also observed.

TBT also causes imposex (the development of male characteristics) in female gastropods, snails and dogwhelks. One of the effects of imposex is the prevention of the release of egg capsules and thus making the females sterile.

Acute poisoning of sensitive aquatic organisms such as algae, zooplankton, molluscs and fish larvae has been demonstrated to occur even at low ng L^{-1} concentrations (Hoch, 2001; Rosenberg, 2005; World Health Organization, 1990).

The potential risk of bioaccumulating OTCs is high for aquatic organisms, because these compounds are easily and rapidly accumulated in algae and in animals by dietary and branchial uptake from water into the lipophilic compartments, whereas their elimination from the body is slow. OTCs are therefore considered to be slow-acting toxic compounds with long-term effects (Cima et al., 2003).

1.1.4.2 Effects on mammals and other terrestrial organisms

In vertebrates, organotins accumulate in specific target organs, i.e. brain, liver, kidney and lymphatic tissues. Metabolites can also be found in these tissues, since the hepatic microsomal system is able to metabolize OTCs by a dealkylation process in mammals.

The use of TBT as wood preservative is the main factor for the exposure of terrestrial organisms. This counts especially for bees that are housed in haves, which are made from treated wood with tributyltin oxide (TBTO), or insects that eat this wood.

The toxicity of TBT to laboratory mammals is moderate to high. The effects include alternations in the blood lipid levels, the endocrine system, liver and spleen and transient deficits in the brain development. TBT vapour/air mixtures do not exhibit any observable toxic effect, even at saturation levels. In contrast to this, TBT is very hazardous as an inhaled aerosol, producing lung irritation and oedema, but has no observable effects for larger animals. TBT is severely irritating to the skin and extremely irritant to the eyes.

Typical symptoms for the exposure to high TBTO concentrations were the loss of appetite, weakness and emaciation. A characteristic toxic effect of TBTO is the suppression of the immune system. The exposure to TBTO in aerosol, leads to a respiratory distress inflammatory reaction within the respiratory tract and histopathological changes of lymphatic organs (Hoch, 2001; Rosenberg, 2005).

1.1.4.3 Effects on humans

The consumption of contaminated drinking water, beverages and, in particular, marine food are possible routes of human exposure to TBT. The presence of DBT in drinking water is coming from PVC pipes. Recent results have shown that fish and fish products are generally the main source of TBT and DBT in the diet.

Also several household commodities composed of polymethane, plastic polymers, and silicones, such as diaper covers, sanitary napkins, certain brands of gloves, cellophane wrap, sponges, and baking parchments, contained amounts (up to the $\mu g\ g^{-1}$ level) of several OTCs (Okoro et al., 2011).

Little is known about the effects of OTCs on humans. Direct exposure to DBT and TBT compounds produce skin irritation or can cause eye irritation after a short contact. Work-related exposure to TPhT acetate has also lead to the observation of effects like sickness, nausea, gastric pain, dryness of the mouth, vision disturbance and shortness of breath for both dermal and inhalation exposure. Currently, no production or use of methyltin and ethyltin compounds exists on an industrial scale, as a result of its high toxicity to humans. The main symptoms of intoxication include a severe headache, vomiting, visual and psychological disturbances and sometimes the loss of consciousness (Hoch, 2001; Rosenberg, 2005; World Health Organization, 1990).

1.1.5 Legislative framework

In the early 1970s, TBT was introduced as an ingredient in marine antifouling coatings for the general use on sea-going vessels. TBT became soon the most cost-effective technology for antifoulant protection of deep-sea vessels. It was so effective that TBT-based antifoulant paint spread to non-essential uses such as pleasure crafts, coastal vessels and freshwater crafts.

1.1.5.1 Legislation

France was the first country that in 1982 banned the use of OTCs in antifouling paints for the application to boats of less than 25 m in length. This ban was due to the collapse of the oyster industry in the Archon Bay in the late 1970s and early 1980s, which was caused by the elevated TBT concentrations in seawater. By the Organotin Antifoulant Paint Control Act, comparable regulations as those imposed in France, were also issued after 1988 in North America, UK, Australia, New Zealand, Hong Kong and most European countries. In this act the use of TBT-containing paints on non-aluminium hulled vessels < 25 m and paints with a leaching rate of more than 4 µg TBT per day were eliminated (Okoro et al., 2011).

In 2001, The International Maritime Organization (IMO), a specialised agency of the United Nations with responsibility for safety and security of shipping and the prevention of marine pollution by ships, acknowledged the harmful effects of organotin antifouling agents and campaigned for a global treaty to ban the application of TBT-based paints. On the 1st of January 2003 the ‘Convention on the control of antifouling systems on ships’ was issued and a total prohibition on the use of TBT took place by January 2008. According to the Convention, all ships should either not have such paints on their surfaces and external parts, or they should have a sealing layer preventing the leaching of such paints (International Convention, 2001; Regulation EC 782/2003, 2003; International Maritime Organisation, 2008; Okoro et al., 2011).

These applied regulations have helped to reduce TBT levels worldwide. Because the premature ban of TBT-based antifouling paints had severe economic consequences to the shipping industry, alternative solutions for antifouling coatings, which are more environmental friendly, should be found (Batt, 2006).

1.1.5.2 Regulatory threshold values for tributyltin in water

Pollution is defined as the exceedance of the relevant Environmental Quality Standards (EQSs) set for the substances in the Directive. An EQS of 1 ng/L for TBT-compounds was set. The EQS was amended in 1997, to a maximum allowed concentration of 2 ng/L for coastal and estuarine water and 20 ng/L for all freshwaters. In 2000, a new maximum concentration threshold has been proposed in the Water Framework Directive 2000/60, lowering the limit to 1.5 ng/L of TBT for all waters (Commision Directive 2000/60/EC, 2000).

1.2 LANDFILLS AND LANDFILL LEACHATES

Increasingly wealthy lifestyles, continuing industrial and commercial growth in many countries around the world in the past decade has been accompanied by rapid increases in both the municipal and industrial solid waste production. Municipal solid waste (MSW) generation continues to grow both in per capita and overall terms (Renou et al., 2008).

MSW is collected by cities and countries and can be separated in three waste streams. Recyclable material is separated by category and then sorted and sold to brokers or vendors. Organic waste can be composted using microorganisms to produce a humuslike substance. The remaining waste stream is placed in a landfill or sent to incinerators, but even incinerations create residue of approximately 10-20 % that must be ultimately landfilled (Chang 2009; Wiszniowski et al., 2006).

Landfills have historically been seen as the ultimate solution for storing waste at minimum costs. Besides its economic advantages, landfilling minimizes environmental hazards and other inconveniences, and allows waste to decompose under controlled conditions until its eventual transformation into a relatively inert, stabilized material (Renou et al.,2008; Krook et al., 2012).

1.2.1 General principle of landfilling

Waste is first tipped into the landfill, compacted and covered with soil to prevent odour, litter, and pest infestations. Typically, municipal landfills consist of about 50-60 weight % of a soil-type material (cover material and heavily degraded waste), 20-30 weight % combustibles (e.g. plastic, paper and wood), 10 % inorganic materials (e.g. concrete, stones and glass) and a few weight % of metals (mainly ferrous metal). This is often the case even when considering landfills in totally different parts of the world. The presence of hazardous waste in the deposits has generally found to be low, often comprising less than one weight % (Krook et al., 2012; Jones, 2015).

The waste will then be gradually decomposed by microorganisms. This decomposition process, mixed with rainwater creates leachates and gas, which are both taken out of the landfill through a system of pipes. The leachates are then usually taken for treatment, while the gas, mainly a mix of carbon dioxide and methane, may be burnt off or used in an on-site energy generation plant. When a landfill has reached its maximum capacity it is covered completely with an engineered cap, e.g. using clay and soils or other covering materials so that the site can be used in the future for agriculture, amenities or nature conservation. (Jones, 2015).

1.2.2 Types of wastes and landfills

A wide variety of wastes are suitable for landfill (Williams, 2005):

Solid hazardous wastes: Solid hazardous wastes are only allowed to be landfilled in hazardous waste landfill sites. Additionally, under the Directive of the European Parliament and of the Council (EC Directive), the waste must be treated before it is landfilled, to reduce the hazardous nature of the waste in terms of the impact on the human health and the environment (Council Directive 1999/31/EC, 1999). Once the treated hazardous waste is placed in the landfill it will be subjected to a range of degradation processes.

Non-hazardous wastes: MSW is the most significant category of waste that is permitted to be deposited in a non-hazardous waste landfill. MSW contains a high proportion of organic material which can be degraded by micro-organisms, which can be found in landfills. MSW includes food and garden waste, paper and fibreboard, wood and some textiles. Provided that they are non-hazardous under the definitions of the Waste Landfill Directive (Council Directive 1999/31/EC, 1999), they would be acceptable in a non-hazardous waste landfill and be subjected to biodegradation processes.

Inert wastes: The major source of inert wastes comes from the construction and destruction industries and mostly consists of bricks, glass, tiles, ceramic materials, concrete, stones, etc. The pollutant content of the waste should be insignificant.Landfills for inert wastes may only accept waste that does not undergo any significant physical, chemical or biological transformations over time, that produce a leachate which contains any pollutants or is ecotoxic. In particular, the properties of the leachate should not endanger the quality of surface water and/or groundwater (Council Directive 1999/31/EC).

There are variations in the design and operation of the landfill:

Conventional landfills: Conventional landfills are designed to entomb solid waste in dry conditions and to minimize the amount of moisture which comes into contact with the waste. Because water will be inevitably present in the waste and some degradation of the waste will occur, these ‘dry tomb’ landfills have engineered liners, to prevent the migration of leachate from the site, and a drainage system, to collect the leachate which accumulated at the bottom of the landfill. Any liquid that is formed, is quickly removed, to prevent the biodegradation and formation of landfill gas (Williams, 2005; Ham and Viste, 1999).

Dry tomb landfilling does little to actually treat or stabilize the waste within the landfill. In this way, dry entombed waste will most probably remain largely unchanged for centuries. As the time period may be many decades or even centuries, the liner materials could fail and release the leachate into the environment. As a consequence, dry tomb landfills must be forever monitored (Williams, 2005; Ham and Viste, 1999).

Bioreactor landfills: A bioreactor landfill is designed and operated to achieve stabilisation of the waste within a 30-50 year time span. The landfill is designed for non-hazardous wastes and, in particular, for biodegradable wastes. This type of landfill significantly increases the extent of organic waste decomposition, conversion rates and process effectiveness in comparison with conventional landfills. This is possible due to continuously recirculation of water and/or leachate through the waste, which flushes out degradation products and replenishes nutrients for the microorganisms. The system for the even distribution of leachate throughout the waste requires a horizontal arrangement of a closely spaced injection pipework, trenches or wells (Williams, 2005; Pacey et al., 2003).

1.2.3 Waste transformation in landfills

When waste is buried in a landfill, a complex series of biological and chemical reactions occur as the waste decomposes. Transformation and degradation mechanisms of organic pollutants gradually change during the ageing of a landfill. With knowledge of these decomposition processes, it is not difficult to understand that most landfills proceed through a series of rather predictable events. Such a sequence has been described by Williams (2005), Kjeldsen et al. (2002) and Heyer and Stegmann (2000). Basically, the sequence can be separated into several distinct phases.

Aerobic phase: During the initial aerobic phase, the oxygen present in the void spaces of the freshly buried waste is rapidly consumed. The aerobic phase in a landfill lasts only from a few days to a few weeks due to the high oxygen demand of waste and the limited quantity of oxygen present inside a landfill.

Hydrolysis and fermentation: As oxygen sources are depleted, the waste becomes anaerobic. The hydrolytic, fermentative and acetogenic bacteria dominate. The anaerobic fermentation reactions result in aminoacids, sugars and volatile fatty acids (VFA) as the main products, which are then further decomposed to organic acids, hydrogen, ammonia and CO_2. The main organic acid is acetic acid, but also propionic, butyric, lactic and formic acids and acid derivative products are formed. The formation of these acids results in a pH decrease.

Acetogenesis: The formed organic acids are converted by acetogen microorganisms to acetic acid, acetic acid derivatives, hydrogen (H_2) and CO_2 under anaerobic conditions. Other organisms convert carbohydrate directly to acetic acid in the presence of H_2 and CO_2.

Methanogenic phase: The onset of the initial methanogenic phase occurs when measurable quantities of methane are produced. This phase is associated with the neutralisation of the pH in the waste, so small amounts of methanogenic bacteria can start to grow. Low levels of H_2 are needed so that these bacteria can covert the generated acids from the acidic phase to methane (CH_4) and CO_2. CH_4 may also be formed from the direct microorganism conversion of H_2 and CO_2. The reactions are relatively slow and it takes many years for their completion.

Maturation phase: In this phase, most of the easily biodegradable wastes have already been decomposed. The landfill has the remaining refractory biodegradables that hardly decompose in anaerobic conditions. Thus, the gas production drops and the leachate strength stays at a constant level. The atmospheric pressure outside the landfill will permeate through the solid waste, resulting to noticeable amounts of nitrogen and oxygen once again. Aerobic microorganisms, which convert residual CH_4 to CO_2 and water, may be established.

The degradation scheme for the organic fraction in a sanitary landfill is presented in Figure 2.

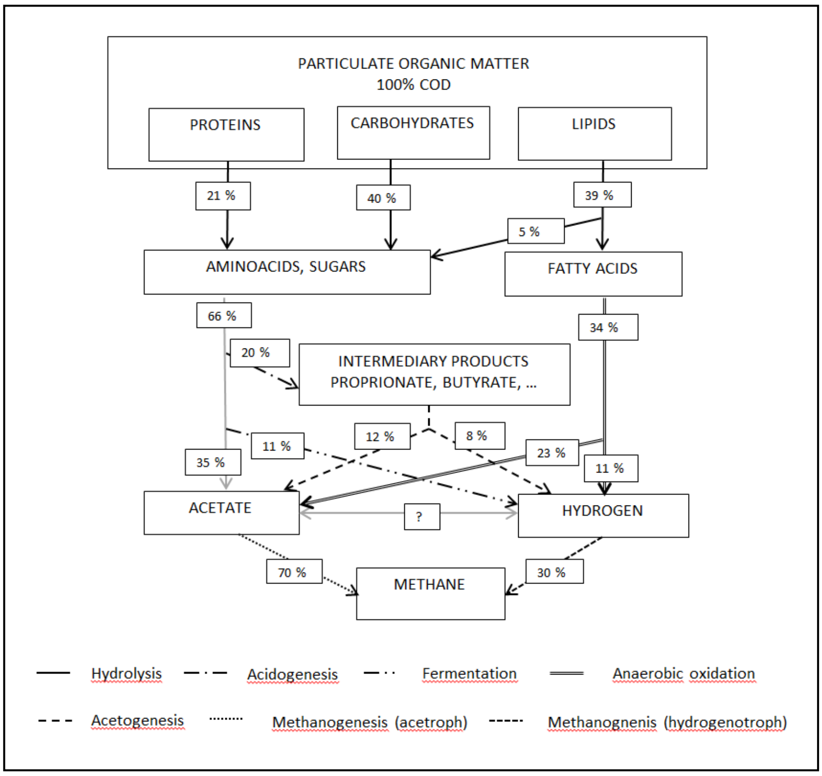

Figure 2: Degradation scheme for the organic fraction in a sanitary landfill. Adapted from ref. Lema et al., 1988.

1.2.4 Formation of landfill gases

Gases arising from the biodegradation of biodegradable wastes in landfills consist of H_2 and CO_2 in the early stages, followed by mainly CH_4 and CO_2 in the later stages. What is known as a ‘landfill gas’, is mainly the product of the methanogenic stage of degradation. The major component of landfill gas is CH_4, which usually comprises 50-55 %, followed by CO_2, which makes up most of the remaining volume. In addition, more than hundred different volatile organic compounds have been identified as trace components, many of which are toxic or caricogenic. Examples are hydrogen sulphide, vinyl chloride, benzene, toluene, trichloroethane and mercaptans (Williams, 2005; McDoughall et al., 2001).

CH_4 has been reported to be responsible for about 20 % of the recent increases in the global warming (Lou and Nair, 2009; McDoughall et al., 2001). To reduce green house gases, the biogas is flared or combusted to generate electricity (Lou and Nair, 2009).

1.2.5 Formation of landfill leachates

A landfill leachate is a liquid flow, induced by gravity force, precipitation, irrigation, surface runoff, rainfall, snowmelt, recirculation, liquid waste co-disposal, waste decomposition, groundwater intrusion and the initial moisture content present within the landfills. When this water infiltrates into the waste layers, it extracts a series of contaminants by a combination of physical, chemical and microbial processes. The results is a liquid, containing suspended solids, soluble components and degradation products(Williams, 2005; Foo and Hameed, 2009).

1.2.6 Composition of landfill leachates

A landfill leachate may be characterized as a water-based solution of four groups of pollutants (Kjeldsen et al., 2002; Foo and Hameed, 2009):

- Dissolved organic matter, VFA (that accumulate during the acid phase of the waste stabilization) and more refractory compounds such as fulvic-like and humic-like compounds.
- Inorganic macrocomponents: calcium (Ca^{2+}), magnesium (Mg^{2+}), barium (Ba^{2+}), sodium (Na^{+}), potassium (K^{+}), ammonium (NH_4^{+}), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^{-}), sulfate (SO_4^{2-}) and hydrogen carbonate (HCO_3^{-}).
- Heavy metals: tin (Sn^{2+} and Sn^{4+}), cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}) and zinc (Zn^{2+}).
- Xenobiotic organic compounds originating from household or industrial chemicals and present in relatively low concentrations (usually less than 1 mg L^{-1} of individual compounds). These compounds include, among others, a variety of OTCs, aromatic hydrocarbons, phenols, chlorinated aliphatics, pesticides and plastizers.
- Other compounds like borate, sulfide, arsenate, selenate, lithium, mercury and cobalt are found in very low concentrations and are only of secondary importance.

1.2.6.1 Transformation of the leachate composition with the age of the landfill

Most of the leachate formed during the aerobic phase, results from the release of moisture during the compaction as well as short-circuiting of precipitation through the buried waste. Young landfills contain large amounts of biodegradable organic matter, which is transformed to organic acids. The presence of the organic acids generates an acidic solution with a pH of 4 or even less. The acidic pH of the leachate increases the solubility of most of the metal ions and thus, increases their concentrations in the leachate. Organic acids, chloride ions, ammonium ions and phosphate ions, which are all present in high concentrations in the leachate, form complexes with metal ions, which further increase their solubilisation (Williams, 2005; Kjeldsen et al., 2002; Kulikowska and Klimiuk, 2008).

When organic acids decompose during the methagonesis, the pH of the leachate increases to a value between 7 and 8. The increase in pH causes a decrease in the solubility of Ca, Fe, Mn and many other heavy metals (Williams, 2005; Kjeldsen et al., 2002; Kulikowska and Klimiuk, 2008).

1.2.6.2 Environmental impacts

The major potential environmental impacts related to landfill leachate are the pollution of ground and surface waters. The risk of groundwater pollution is probably the most severe environmental impact from landfills because, historically most landfills were built without engineered liners and leachate collection systems. More recently, regulations in many countries have required the installation of liners and leachate collection systems, as well as a plan for leachate treatment. The major potential hazards of a leachate entering the nearby environment, are the release of contaminants to surface water, oxygen depletion, changes in the stream bottom fauna and flora and ammonia toxicity (Kjeldsen et al., 2002).

1.2.6.3 Treatment of landfill leachates

As a result of the variable leachate compositions from different landfills, leachate treatment methods have not been unified so far. For managers of landfill sites, it is important to fully understand the on-going processes, as well as to have knowledge about the occurrence and the behaviour of contaminants, which are present in the leachate (Kulikowska and Klimiuk, 2008).

The combined treatment with domestic sewage was preferred for its easy maintenance and low operating costs. However, due to the presence of organic compounds with low degradability and heavy metals in leachates, the efficiency of this treatment is questionable (Renou et al, 2008).

Recycling of the leachate, back into the landfill is one of the least expensive options available. It increases the moisture content and provides the distribution of nutrients and enzymes. It not only improves the leachate quality, but also shortens the time for stabilisation. On the other hand, leachate recirculation may cause high concentrations of organic acids which are toxic for methanogenic bacteria (Renou et al., 2008).

Due to its reliability, simplicity and high cost-effectiveness, biological treatment is commonly used. Biodegradation is carried out by microorganisms, which can degrade organic compounds (Renou et al., 2008; Poland and Harper, 1987).

Physical and chemical processes include precipitation, coagulation, ion exchange, adsorption and chemical oxidation (Renou et al., 2008; Poland and Harper, 1987).

Conventional treatments are not sufficient anymore to reach the level of purification needed to fully reduce the negative impact of landfill leachates on the environment. That is why treatments based on membrane technology have emerged as a viable treatment alternative to comply with the water quality regulations in most countries (Renou et al., 2008).

1.3 ORGANOTIN COMPOUNDS IN LANDFILLS AND LANDFILL LEACHATES

Many investigations confirmed that there are, even after the ban of TBT in antifouling paints, still detectable levels of OTCs present in household products and plastic materials (Pinel Raffaitin et al., 2008). Therefore, MSW that is collected on landfills can be considered as an important pool of OTCs. Landfills gather the conditions, enhancing the chemical and biological transformation of tin. In this way, inorganic tin and OTCs present in the waste can be modified by hydridation, methylation, ethylation, dealkylation or transalkylation reactions, with the consequence of generating new tin compounds in both liquid and gaseous phases. The environmental impact of landfill leachates and biogases could thus change during the waste biodegradation. In contrast to dealkylation processes, which decrease the toxicity of the OTCs, methylation pathways enhance their toxicity. Due to these transformation processes, the release of major contaminants from the landfill into the atmosphere or aquatic ecosystem are still scarcely documented (Pinel Raffaitin et al., 2008).

1.3.1 Pahtways of organotin compounds in landfills

There are several pathways of OTCs in landfills: The substances may be retained in the solid waste matrix (e.g. OTC stabilizers fixed in rigid PVC products). The target compounds may be transported by the leachate or may be volatilized into the landfill gas (Mersiowsky et al., 2001).

In different investigations on the occurrence of OTCs in leachate samples, the following species were identified: MMeT, DMeT, TMeT, monoethyltin, diethyltin, MBT, DBT, TBT, monooctyltin and dioctyltin. Among them, TMeT dominated (Mersiowsky et al., 2001; Pinel-Raffaitin et al., 2007; Ilgen et al., 2008; Vahčič et al., 2011a). TBT and DBT mainly originated from the disposed waste products or sewage sludge, which is often co-disposed with municipal solid waste in sanitary landfills (Mersiowsky et al., 2001), while DBT and MBT can be formed also through degradation process in the leachate. The occurrence of MMeT, DMeT and TMeT is mainly related to methylation by microorganisms (Ilgen et al., 2008; Rosenberg, 2005).

In landfill gases volatile tetramethyltin (TeMeT) predominates, representing more than 80 % of total gaseous Sn. Volatile ethyltins and methyl-ethyltin species were also present in the landfill gases (Ilgen et al., 2008).

In pipes, which transport landfill gases, a condensate of water occurs. Volatile TeMeT is demethylated to TMeT and transferred into the aqueous condensate. Since this condensate is returned back to the landfill leachate, the TMeT species is the predominant OTC in the leachate (Ilgen et al., 2008).

The scheme of the transformation processes of OTCs under landfill conditions is shown in Figure 3.

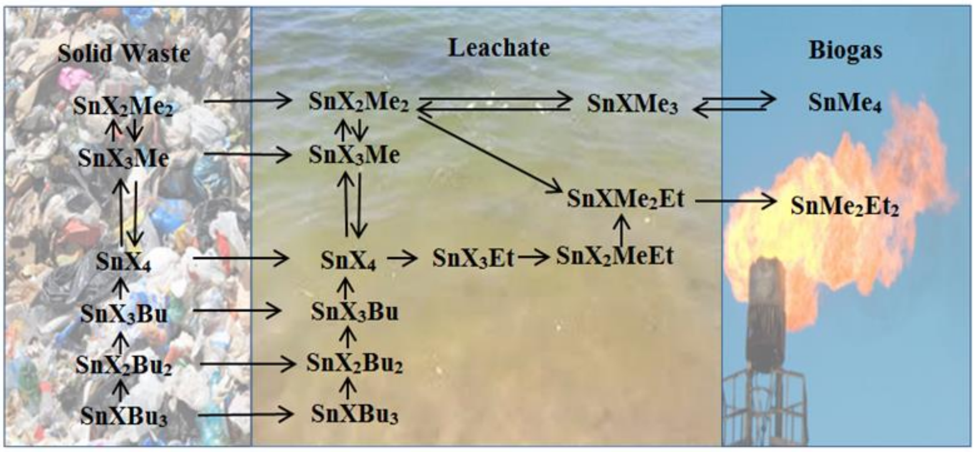

Figure 3: Transformation of OTCs under landfill conditions. Adapted from ref. Pinel-Raffaitin et al., 2007.

1.3.2 Remediation of organotin compounds in landfill leachates

OTCs may be present in landfill leachates in concentrations that are toxic to most of the sensitive organisms. In landfill leachates, the biotic and abiotic degradation of OTCs occurs naturally (Peeters et al., 2014). So, before leachates are released in the environment, they first have to be treated.However, this degradation is not sufficient to prevent environmental pollution. Due to that reason, researchers are looking for alternative solutions to remove OTCs by flocculation, the use of adsorbents, bacteria, or nanoparticles (NPs) (Ayanda et al., 2012). Each treatment has its own specific disadvantages.

- Degradation by microorganisms or their active components is expensive, takes a long time and is only possible if the concentration of OTCs is not too high.
- The method of adsorbing OTCs onto a polyethylene sheet, active carbon, clay or polyamide substance has many processing steps and is also expensive.
- The system of irradiating water with ozone and UV light needs complex and expensive treatment apparatus.
- Flocculation can work for TBT because it is readily adsorbed to suspended particles but it’s not a solution for TMeT, which stays mainly in solution.

In general can be concluded that most of the methods tend to be expensive and cannot be used on industrial scale. Therefore, there is a need for remediation processes that are cheap, easy to handle and will effectively remove OTCs from the aquatic environment (Honda and Takahashi, 2008; Ayanda et al., 2012).

2 AIMS AND HYPOTHESIS

OTCs are among the most hazardous pollutants, known so far, to have ever been introduced into aquatic ecosystems by man. Landfill leachates are an important pool of these toxic substances.

In order to prevent their release to the nearby environment, it is first of all important to understand the transformations that OTCs undergo in landfill leachates. To follow these transformation processes, Sn-enriched isotopes represent a powerfool analytical tool. Hovewer, Sn-enriched DBT, TBT and ionic tin, which would enable such investigations, are not commercially available as single species.

It is also important to apply appropriate remediation procedures. Iron nanoparticles are widely used for cost-effective remediation of polluted environmental waters. Nevertheless, they have not been applied to remediate OTCs in complex matrices such as landfill leachates. There is also a lack of information available on the fate of iron nanoparticles (FeNPs) after the treatment of environmental waters.

In order to contribute to a comprehensive knowledge on the transformation processes of OTCs in landfill leachates and to evaluate the potential of removal of OTCs by FeNPs, the aims of the present doctoral thesis were:

- The‘‘In house’’synthesis of individual ^{117}Sn-enriched TBT, ^{119}Sn-enriched DBT, ^{117}Sn-enriched $SnCl_2$ and ^{117}Sn-enriched $SnCl_4$ from Sn-enriched metallic tin.

- The investigation of the degradation and biomethylation of OTCs in leachate under simulated landfill conditions over a time span of six months, using Sn-enriched isotopic tracers. For discriminating between biotic and abiotic transformations of OTCs and inorganic tin species, the data between concentrations of OTCs in sterilized and non-sterilized leachate samples were compared.

- The investigation of the conditions for the effective removal of OTCs from landfill leachates by FeNPs, namely nanozerovalent iron (nZVI), iron oxide nanoparticles

(FeONPs) and magnetite nanoparticles (Fe_3O_4NPs), with a special emphasis on the removal of TBT and TMeT. TBT is one of the most toxic OTCs and is, despite its global ban, still present in the marine and terrestrial environment, while TMeT is neurotoxic and occurs in notable concentrations in landfill leachates.

- The study of the fate of FeNPs after the treatment of environmental waters, which differ in ionic strength and the content of organic matter, by nZVI, FeONPs and Fe_3O_4NPs. The efficiency of the removal of selected metals was also evaluated in forest spring water and landfill leachate.

3 FRAME OF THE DOCTORAL THESIS

The doctoral thesis is composed of four parts, which are comprehensively integrated to bring new knowledge on the transformation and behaviour of OTCs in landfill leachates and the possibilities of their removal from the leachate by the use of FeNPs.

- In the first part, the synthesis of individual Sn-enriched OTCs and ionic tin species from Sn-enriched metallic tin is presented.
- In the second part, these synthesized Sn-enriched species were used to investigate the degradation and biomethylation of OTCs in the leachate under simulated landfill conditions over a time span of six month.
- In the third part, the conditions for the efficient removal of TBT and TMeT from the landfill leachate by the use of different FeNPs (nZVI, FeONPs and Fe_3O_4NPs) were studied.
- In the fourth part, the fate of nZVI, FeONPs and Fe_3O_4NPs was investigated after the treatment of environmental waters, which differ in ionic strength and the content of organic matter. The efficiency of the removal of selected metals was also evaluated in forest spring water and landfill leachate.

According to the order of the parts of the doctoral thesis, an extended literature survey and the fundamentals of isotope dilution are presented.

3.1 LITERATURE SURVEY ON THE SYNTHESIS OF Sn-ENRICHED ORGANOTIN COMPOUNDS

OTCs are common pollutants in marine ecosystems (Amouroux et al., 2000; Ščančar et al., 2007; Milivojevič Nemanič et al., 2009; Furdek et al., 2012) but are also present in the terrestrial environment (Zuliani et al., 2006), mainly accumulated in sewage sludge (Zuliani et al., 2008; Zuliani et al., 2012) and landfill leachates (Mersiowsky et al., 2001; Pinel-Raffaitin et al., 2007; Pinel-Raffaitin et al., 2008; Vahčič et al., 2011a). In investigations of the degradation and methylation processes of OTCs in environmental samples, the use of enriched isotopic tracers represents a powerful analytical tool. Sn-enriched OTCs are also necessary in the application of the isotope dilution (ID) mass spectrometry technique for their accurate quantification (Rodrígues-Gonzáles et al., 2005). Different approaches were reported to synthesise butyltin species.

Isotopically enriched OTCs were prepared from a metallic plate of isotopically enriched tin. Ruiz Encinar et. al. (2001) synthesised a mixed ^{119}Sn-enriched butyltin spike (MBT, DBT and TBT) by the direct butylation of ^{119}Sn-enriched tin metal using a 1:3 molar excess of butyl chloride with iodide and triethylamine as catalysts. Similarly, the direct butylation approach was applied for the preparation of a mixture of ^{118}Sn-enriched butyltin compounds by mixing n-butyl iodide with n-butanol and the addition of ^{118}Sn metal and lithium metal (Inagaki et al., 2003). Attempts were also made to synthesise individual OTC-enriched species (Inagaki et al., 2007; Ruiz Encinar et al., 2000; Sutton et al., 2000). Ruiz Encinar and co-workers (2000) prepared ^{118}Sn-enriched DBT by the reaction of ^{118}Sn metal with butyliodide, using dimethylformamide as a polar solvent and tetrabutylammonium iodide as a phase transfer catalyst. Synthesis of Sn-enriched MBT was not performed directly (Rodrígues-Gonzáles et al., 2004), but MBT was isolated from a previously synthesized ^{119}Sn-enriched spike (Ruiz Encinar et al., 2001) by the removal of the more volatile TBT and DBT under a gentle stream of argon and the purification of MBT by semi-preparative high pressure liquid chromatography. Preparation of isotopically Sn-enriched DBT dichloride, TBT chloride, TBT iodide, as well as diphenyltin (DPhT) dichloride, TPhT chloride and TPhT iodide based on the reaction of isotopically enriched metallic tin with iodine, followed by the reaction between SnI_4 and the corresponding tetraorganotin was also reported (Sutton et al., 2000). All these procedures were quite complicated since they required numerous reactions and purification steps. The only exception was the preparation of DBT diiodide, which was synthesized directly by reacting tin metal and iodobutane.

Currently, among Sn-enriched OTCs, only the ^{119}Sn-enriched butyltin mix supplied by ISC Science (Oviedo, Spain) is commercially available. So, to obtain individual Sn-enriched OTCs, “in house” synthesis is needed. The high cost of the starting material for the synthesis of isotopically enriched OTCs makes the use of small quantities necessary (Ruiz Encinar et al., 2000). Successful synthesis of Sn-enriched OTCs on a micro-scale requires the use of stable reagents, easy isolation of each reaction product and a minimal number of synthetic and purification steps. It is also desirable to have high reaction yields for each step.

In this view, it was necessary to develop a simple procedure for the preparation of ^{117}Sn-enriched TBT from ^{117}Sn metal on a micro-scale and to characterize the product by speciation analysis.

3.1.1 Fundamentals of isotope dilution

Isotope dilution (ID), as a primary chemical method allows, when correctly implemented, the accurate determination of elemental concentrations. It is a well-known analytical technique based on the measurement of isotope ratios in samples, in which the isotopic composition has been altered by the addition of a known amount of an isotopically enriched element. The element to be analysed must have, therefore, at least two stable or long-lived radioactive isotopes able to be measured in a mass spectrometer and be free of spectral interferences (Rodrígues-Gonzáles et al., 2005; Garcia Alonso and Rodrígues-Gonzáles, 2013).

One of the applications of ID is its use in the field of elemental speciation, where the aim is to determine the individual chemical species in which an element is distributed in a given sample (Rodrígues-Gonzáles et al., 2005; Garcia Alonso and Rodrígues-Gonzáles, 2013).

Advantages of ID over other calibration techniques are the following:

- ID analysis compensates for instrumental instabilities such as signal drift or matrix effects.
- The uncertainty in the concentration measurement depends only on the uncertainty in the measurement of the isotope ratios.
- Once the isotope equilibration between the sample and the spike has been achieved, possible losses of substances of the isotope-diluted sample will have no influence on the final result.
- There is no need for external calibration to calculate the concentration of the analyte, which is an advantage in terms of the necessary time to complete the analytical procedure.

For the accurate quantification of OTCs and the validation of analytical methods, the species-specific ID mass spectrometry technique is applied. To determine the concentrations of Sn-enriched OTCs, the species-specific reversed ID mass spectrometry technique is used. Reverse ID refers to exactly the same process as ID, but the isotopic spike is considered as the sample and the standard solution with a natural isotopic composition as the spike (Vanhaecke and Degryse, 2012).

In the present doctoral thesis, the accurate concentration of the synthesized ^{117}Sn-enriched TBT (^{117}TBT) was calculated by reversed ID-GCICPMS.

The schematic presentation of reverse ID for the determination of the ^{117}TBT concentration is shown in Figure 4.

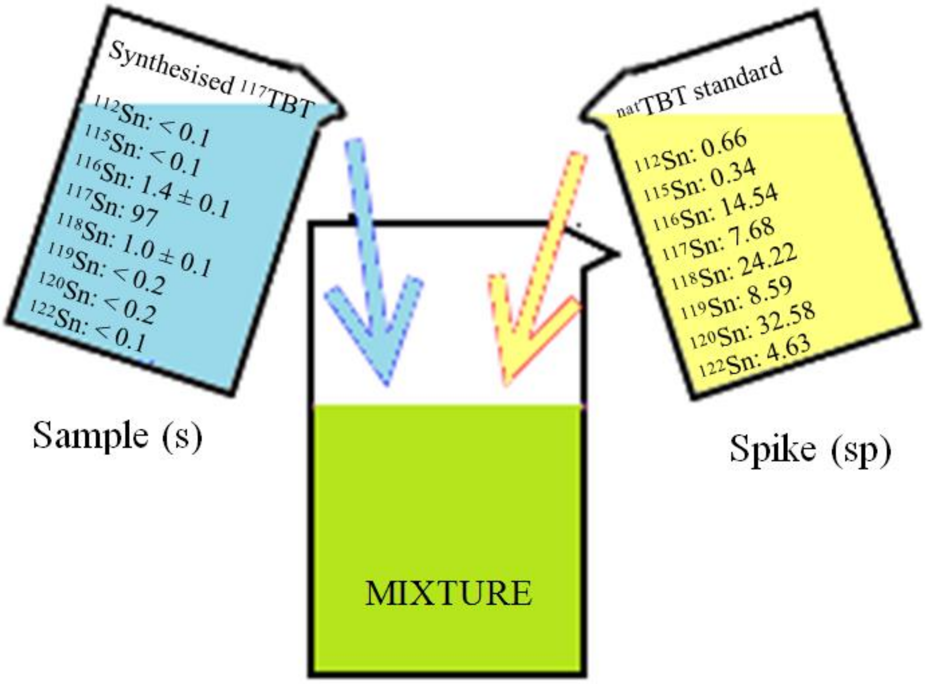

Figure 4: Schematic presentation of the principle of reverse ID for the determination of the concentration of ^{117}TBT.

The formula for the calculation of ^{117}TBT by reversed ID is expressed in equation [1] (Rodrígues-Gonzáles et al., 2005; Garcia Alonso and Rodrígues-Gonzáles, 2013).

$$c_s = c_{sp} \frac{m_{sp}}{m_s} \frac{M_s}{M_{sp}} \frac{A_{sp}^b}{A_s^a} \frac{R_m - R_{sp}}{1 - R_m R_s} \qquad [1]$$

a is the measured Sn isotope at *m/z* 117.

b is the measured Sn isotope at *m/z* 120.

R_m is the isotope ratio of the ^{117}Sn and ^{120}Sn isotopes in the mixture.

A_s^a and A_s^b are the isotopic abundances for the isotopes a and b in the samples, while A_{sp}^a and A_{sp}^b are those in the spike.

$R_s = (A_s^b)/(A_s^a)$ is the isotope ratio (b/a) in the sample.

$R_{sp} = (A_{sp}^a)/(A_{sp}^b)$ is the isotope ratio (a/b) in the spike.

c_s and c_{sp} are the concentrations of the element in the sample and the spike, respectively.

m_s and m_{sp} are the masses taken from the sample and the spike, respectively.

M_s and M_{sp} are the elemental atomic weights of Sn in the sample and the spike, respectively.

3.2 LITERATURE SURVEY ON THE TRANSFORMATION OF ORGANOTIN COMPOUNDS IN LANDFILL LEACHATES

The collection of municipal waste on landfill sites is one of the most commonly employed waste management systems worldwide. A landfill can be considered to be an important pool of OTCs as a result of their presence in plastic materials, manufactured household products and cans for food packing. Both OTCs and inorganic tin can be mobilised by percolation of water through the waste pile. To prevent the water that percolates through the waste from coming into contact with surface or groundwater, a pond is constructed to collect the landfill leachate. The environment in landfills generate conditions for the chemical and biological modifications of inorganic tin and OTCs, which can be transformed by hydridation, methylation, ethylation, dealkylation or transalkylation reactions (Amouroux et al., 2000; Pinel-Raffaitin et al., 2008). This results in the formation of new tin compounds in landfill leachates and biogases (Pinel-Raffaitin et al., 2008; Ilgen et al., 2008; Vahčič et al., 2011a). The release of OTCs from landfill leachates into the aquatic ecosystem or atmosphere is still scarcely documented. In order to prevent environmental pollution, there is a need for the estimation of the ecological impact of OTCs, since tin was found as one of the main leachate contaminants among the metals and metalloids (Pinel-Raffaitin et al., 2008). The use of enriched isotopes can provide comprehensive information in the investigations of the transformation of OTCs in environmental samples. Nevertheless, they were rarely applied in studies of the fate of OTCs in landfill leachates, but were only used for the quantification of alkyltin species in these samples via ID-GC-ICPMS by the addition of a ^{119}Sn-enriched butyltin mix spike containing MBT, DBT and TBT (Pinel-Raffaitin et al., 2007).

Microorganisms may significantly influence the transformation processes of OTCs in landfill leachates, so it is important to study the pathways of the degradation and/or formation of newly formed OTCs. In previous studies, the occurrence of OTCs in leachates from the landfill in Barje, Slovenia, was investigated (Vahčič et al., 2011a). The data revealed that the prevailing OTCs, found in leachates, were methyltin and butyltin species.

To better understand the processes that OTCs undergo in leachates, the degradation and biomethylation of these OTCs in leachate were followed in the present doctoral thesis, by the use of "in house" prepared isotopically enriched tin tracers, namely: ^{117}Sn-enriched $SnCl_2$, ^{117}Sn-enriched $SnCl_4$, ^{117}Sn-enriched TBT, ^{119}Sn-enriched DBT, and a commercially available ^{119}Sn-enriched butyltin mix containing TBT, DBT and MBT.

3.3 LITERATURE SURVEY ON THE REMOVAL OF POLLUTANTS FROM ENVIRONMENTAL WATERS BY NANOPARTICLES

Management of municipal solid wastes is required to prevent the release of pollutants like OTCs from treatment and disposal facilities. In 2006, the European Commission approved a Council Directive on the 'Landfill of Waste', with the aim to reduce the negative effects of pollutants on the environment (Directive 2006/12/EC, 2006). To prevent environmental pollution with OTCs, researchers are looking for solutions to remove them from contaminated waters such as by flocculation and/or the use of various adsorbents. Recently, NPs have received significant interest for environmental remediation (Joo and Cheng, 2006). Nanotechnology provides opportunities for the efficient remediation of contaminated soil (Machadoa et al., 2013) and environmental waters (Kamat and Meisel, 2003; Zhang and Surampalli, 2009). Some of the main advantages for its in situ soil, groundwater and surface water remediation include the high degree of the NPs reactivity, the cost-effectiveness, the access to hard-to-reach sites, shorter clean-up times and the possibility of subsequent injections (Grieger et al, 2010).

Many different nanoscale materials have been explored for remediation, such as nano-scale zeolites, metal oxides, carbon nanotubes and fibers, enzymes, various noble metals (mainly as bimetallic nanoparticles), and titanium dioxide (Zhang, 2003; Zhang and Surampalli, 2009). Of these, magnetic FeNPs (nZVI, FeONPs and Fe_3O_4NPs) represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental clean-up problems (Lo et al., 2009; Shen et al., 2009). FeNPs are magnetic nanoparticles with large surface areas and high surface reactivity. They provide high flexibility for in situ applications. Research has shown that FeNPs are very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes, polychlorinated hydrocarbons, pesticides and dyes (Zhang, 2003; Tratnyek and Johnson, 2006; Karn et al., 2009).

3.3.1 Principles of the removal of pollutants from environmental waters by iron nanoparticles

At neutral to alkaline pHs, the adsorption of pollutants onto the surface of FeNPs and the co-precipitation with iron corrosion products is the main process of pollutant removal (Noubactep, 2010). After remediation, the iron precipitate can be simply taken away by a magnet. At acidic pHs, in aerated solutions containing dissolved Fe^{2+} and organic ligands like citrate, oxalate or EDTA, a Fenton-type reaction takes place through a series of ligand-mediated reactions, resulting in the formation of hydrogen peroxide (H_2O_2) and highly reactive hydroxyl radicals ($OH^{\bullet}$). $OH^{\bullet}$ are strong oxidants, which are capable to rapidly degrade many organic and inorganic compounds (Deng and Englehardt, 2006; Gylienė et al., 2008; Keenan and Sedlak, 2008; Zhou et al., 2009; Zhou et al., 2010; Martins et al., 2012; Babuponnusami and Muthukumar, 2014). To initiate a Fenton-type reaction with FeNPs, citrate can be used as an environmental friendly alternative for toxic ethylenediaminetetraacetic acid (EDTA) (Gylienė et al., 2007). Iron forms stable complexes with citrate that generate the superoxide radical $O_2^{\bullet-}$, which by further reaction with Fe-complexes produces H_2O_2. H_2O_2 is a source for the Fenton process that yields $OH^{\bullet}$ radicals.

It is expected that a Fenton type reaction will take place through a series of reactions, which can be recorded by the equations [2-6] as proposed by Gylienė et al. (2008), where L represents a citrate ligand.

$$Fe^0 \rightarrow Fe^{2+} + 2\ e^- \quad [2]$$

$$Fe^{2+} + L \rightarrow Fe^{2+}L \quad [3]$$

$$Fe^{2+}L + O_2 \rightarrow Fe^{3+}L + O_2^{\bullet -} \quad [4]$$

$$Fe^{2+}L + O_2^{\bullet -} + 2H^+ \rightarrow Fe^{3+}L + H_2O_2 \quad [5]$$

$$Fe^{2+}L + H_2O_2 \rightarrow Fe^{3+}L + OH^{\bullet} + OH^- \quad [6]$$

The pH is a key parameter in Fenton-like processes. As the pH rises, the production of $OH^{\bullet}$ radicals is decreased, due to formation of iron corrosion product precipitates (Martins et al., 2012).

The biotic and abiotic degradation of toxic OTCs in landfill leachates is usually not complete. To find out whether FeNPs can remove these pollutants from the leachate, the processes of adsorption and degradation of TBT and TMeT in landfill leachates treated with different FeNPs (nZVI, FeONPs and Fe_3O_4NPs) were investigated in the doctoral thesis. TBT was chosen since it is one of the most toxic OTCs and is, despite its global ban (International Convention, 2001), still present in the marine (Furdek et al., 2012) and terrestrial environment (Silva et al., 2014), while TMeT is neurotoxic (Huong et al., 2011) and occurs in notable concentrations in landfill leachates.

3.4 LITERATURE SURVEY ON THE BEHAVIOUR OF OF IRON NANOPARTICLES IN ENVIRONMENTAL WATERS

Among the different NPs, which are used in the remediation of contaminated environmental waters, FeNPs are the most frequently applied. If FeNPs remain in these waters after the treatment, they can cause hazardous effects to the environment. Despite the concern of their potential environmental or toxicological impacts, there are only a few studies that investigated the toxicological effects of FeNPs on living organisms (Auffan et al., 2008; Grieger et al., 2010; Karthikeyeni et al., 2013; Mauer-Jones et al., 2013). Cytotoxic effects of Fe_3O_4NPs and nZVI towards *E. Colli* occurred for doses higher than 700 mg/L and 70 mg/L, respectively

(Auffan et al., 2008). For the fish species *Oryzias Latipes*, nZVI caused a disturbance in the oxidative defence system at concentrations as low as 0.5 mg/L. In its adult stage, the fishes showed histopathological changes, morphological alterations on gills and intestines, and antioxidant balance disruption, although they were able to recover afterwards. For the other fish species *Pimephales promelas*, 50 mg/L nZVI causes some changes in the gene regulation, including genes that encode proteins involved in tissue repair and in antioxidant defences. Acute toxicity to aquatic organisms appears to be relatively low, although sub-lethal effects have been observed (Grieger et al., 2010).

When FeNPs are used for environmental water remediation, NPs may persist in solution after the treatment. The aggregation of FeNPs is highly dependent on the ionic strength and the content of natural organic matter (Jiang et al., 2009; Hotze et al., 2010). To estimate the potential toxic effects of the remaining FeNPs towards biota, it is necessary to study their behaviour after the treatment. Therefore, in the doctoral thesis the fate of nZVI, FeONPs and Fe_3O_4NPs was investigated in Milli Q water, forest spring water and landfill leachate, which differ in ionic strength and the content of organic matter.

4 MATERIALS AND METHODS

4.1 MATERIALS

The standards for quantification, of MBT trichloride (95 %), TBTCl (96 %) and tetrabutyltin (TeBT, 93 %) were purchased from Aldrich (Milwaukee, WI, USA). MMeT trichloride (98 %), DMeT dichloride (95 %) and TMeT chloride (99 %) were purchased from Acros Organics (New Jersey, NY, USA). DBT dichloride (98 %) and tripropyltin (TPrT) chloride (98 %) were obtained from Merck. OTC standard stock solutions containing 1000 mg L^{-1} (expressed as Sn) were prepared in methanol and stored in the dark at 4 °C. Working OTCs standard solutions were prepared daily. The ^{119}Sn-enriched butyltin mix was obtained from ISC Science (Oviedo, Spain).

For ICPMS analysis, sodium acetate was purchased from Carlo Erba and acetic acid from Sigma Aldrich. Hexane, isooctane and methanol came from J.T. Baker (Deventer, Holland). Citric acid monohydrate (p.a.) and Tris (hydroxymethyl)aminomethane (Tris) (p.a.) were obtained from Merck (Darmstadt, Germany). Sodium tetraethyl borate ($NaBEt_4$, 98 %) was used from Strem Chemicals (Newburyport, MA, USA). An aqueous solution of $NaBEt_4$ (2 % (w/v)) was prepared just before derivatization. The acetate or Tris-citrate buffer was prepared weekly. Milli-Q water (18.2 MΩcm), obtained by Direct-Q 5 Ultrapure water system (Milipore, Bedford, MA, USA), was used for the preparation of all aqueous solutions.

To synthesize TBT, the following products were purchased: Sn powder (particle size < 71 µm) and bromine from Merck (Darmstadt, Germany), anhydrous diethyl ether, acetonitrile, anhydrous sodium sulphate and a 2.5 mol L^{-1} solution of butyllithium (BuLi) from Aldrich (Steinheim, Germany). Diethyl ether and hydrochloric acid were purchased from Applichem (Darmstadt, Germany). Methanol came from Carlo Erba (Milan, Italy). To prepare ^{117}Sn-enriched TBT, the Sn powder was changed with a ^{117}Sn-metal plate (97 % of ^{117}Sn) (Cambridge Isotope Laboratories Inc., MA, USA). All the used reagents were of analytical-reagent grade.

To prepare the solution for NMR analysis, deuterated chloroform and tetramethylsilane were used, which were purchased from Eurisotop (Saint-Aubin, France).

Merck (Darmstadt, Germany) suprapur acids and Milli Q water were used for the preparation of samples and standard solutions. All other chemicals were of analytical reagent grade. Stock Multi Element XVI standard solution (100 mg L^{-1} in 5 % HNO_3) (Merck, Darmstadt, Germany) was used for the preparation of working standard solutions for ICPMS determinations.

Magnetic nZVI (manufactural size information approximately 25 nm), stabilized with a layer of FeO, was obtained from MKNano, (Williamsville, NY USA). The magnetic FeONPs, stabilized with a layer of oleic acid and kept in heptane (particle size 3.5 - 9.5 nm), and magnetic Fe_3O_4 nanopowder (particle size < 50 nm), were purchased from Sigma-Aldrich (Steinheim, Germany) (Fig. 5). Tertramethylammonium hydroxide (TMAH) (25 wt % in methanol), used for the dispersion of FeNPs, came also from Sigma-Aldrich.

The particle sizes of nZVI, FeONPs and Fe_3O_4NPs were verified by transmission electron microscopy (TEM) and are presented in Fig. 5.

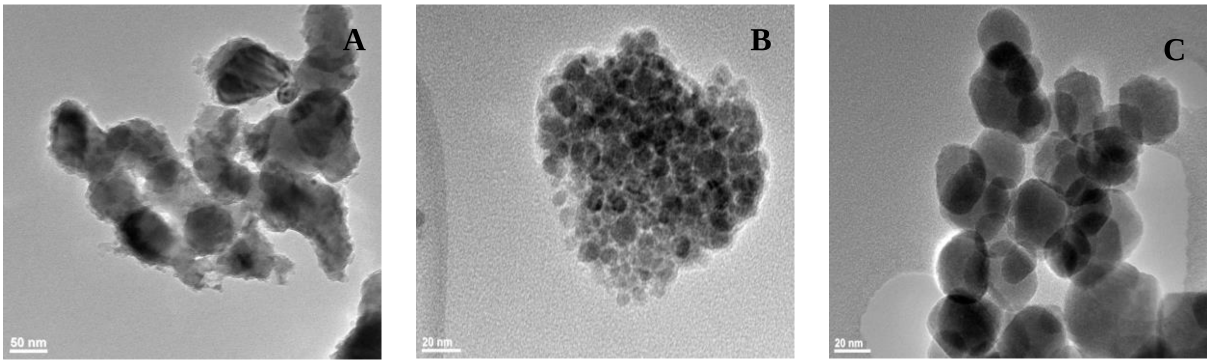

Fig 5: Particle sizes of (A) nZVI, (B) FeONPs and (C) Fe_3O_4NPs. The images were made by TEM analysis.

Data from Fig 5 indicate that nZVI (Fig. 5A) makes agglomerates between 50 and 100 nm, which contain smaller particles whit sizes from approximately 10 to 25 nm. From Fig. 5B it is seen that FeONPs in general contain particles smaller than 10 nm, while dta from Fig. 5C show that Fe_3O_4NPs contain particles below 50 nm. These data are in accordance with the manufacturers' information.

For sequential filtration of aqueous samples, 5 µm cellulose-nitrate, 0.45 µm, 0.2 µm and 0.1 µm cellulose-acetate membrane filters and 10 KDa regenerated cellulose filters (2.5 nm) were obtained from Whatman (Vienna, Austria), Ministart (Goettingen, Germany) and Amicon (Zagreb, Croatia), respectively.

4.2 INSTRUMENTATION

The determination of OTCs was carried out on an Agilent 6890 gas chromatograph (GC) (Agilent Technologies, Santa Clara, CA, USA) equipped with an Agilent 6890 Series Autosampler Injector that was coupled to an Agilent 7700x ICPMS (Agilent Technologies, Tokyo, Japan) via a heated transfer line and fitted with a 15 m × 0.25 mm DB- 5MS capillary column (film thickness 0.25 µm) coated with 5% phenyl-methylpolysiloxane (Agilent J&W Scientific, Palo Alto, CA, USA). The control and operation of the coupled system was achieved by using Agilent ChemStation Software.

NMR spectra were recorded with an Agilent (Palo Alto, CA, USA) Inova 300 spectrometer (300 MHz). The samples were dissolved in deuterated chloroform and tetramethylsilane was used as an internal standard.

Mechanical shaking of the samples was performed on an orbital shaker Vibromix 40 (Tehtnica, Železniki, Slovenia).

A Mettler-Toledo EasyMax Synthesis Workstation (Columbus, OH, USA) was used to maintain the temperature in controlled conditions during the chlorination process to produce TBT out of TeBT.

Micrographs were made on 200 kV transmission electron microscope Jeol JEM-2100 with W filament. Particles were dissolved in absolute ethanol, sonicated and then a drop of solution was transferred onto a copper carbon-lacy grid.

The sterilization of leachate samples was performed for 2 hours at 121 °C in an autoclave Getinge GE6610EM-2 (Getinge, Sweden).

4.3 METHODS

4.3.1 Sampling of landfill leachates and forest spring water

Sampling of leachates was performed in the non-hazardous municipal waste landfill in Barje, Ljubljana, Slovenia. The surface of the waste disposal area is 49.300 m^2 and has a capacity of 884.000 m^3. 30 L of sample was taken from a leachate control well of the active landfill basin by an aluminium bucket, from the bottom of the well, poured into a 30 L polyethylene bottle and was directly transported to the laboratory.

Sampling of the unpolluted forest spring water was performed at the rivulet Hruševnik close to Ljubljana city, Slovenia.

4.3.2 Analytical procedure for the determination of ^{117}Sn-enriched tributyltin chloride and organotin compounds in landfill leachates by GC-ICPMS

To determine the concentration of the synthesised ^{117}TBTCl, an aliquot of standard, which was prepared in methanol, was appropriately diluted in 100 mL of Milli Q water. The speciation analysis was carried out under a previously optimised procedure (Vahčič et al., 2011b). A 100 mL aliquot of water sample was transferred into 500 mL dark glass reactor vessels along with 100 mL of a sodium acetate – acetic acid buffer solution (pH 4.8). The sample was spiked with an internal standard solution of TPrT. To the spiked sample, 0.5 mL of 2 % (m/V) $NaBEt_4$, for derivatisation, and 1 mL of iso-octane, as an extraction agent for ethylated OTCs, were added. The samples were mechanically shaken for 45 min and after that, the organic phase was collected for the analysis into 2 mL dark vials using a Pasteur pipette. The speciation analysis was performed by GC-ICPMS.

For the separation of OTCs, using a 15 m column, the following GC temperature program was applied: at the start, the column temperature was held at 50 °C for 0.8 min, then it was raised to 200 °C at a heating rate of 20 °C min^{-1} and held there for 2 min, then it was raised to 220 °C at a heating rate of 40 °C min^{-1} and held there for 0.5 min. In the final step, the temperature was raised to 280 °C at a heating rate of 50 °C min^{-1} and held at this temperature for 2 min. The inlet temperature was 240 °C and the transfer-line was held at 280 °C. Helium, at a flowrate of 1 mL min^{-1} was used as a carrier gas. A spitless injection mode was used with an injection volume of 2 µL. The instrumental parameters for the GC-ICPMS measurements are given in Table 2 (Vahčič et al., 2011a).

Table 2: Instrumental parameters of the GC and ICPMS.

ICPMS	***Agilent 7700x***
RF power	1500 W
Sample depth	7.2 mm
Carrier gas	0.69 L min^{-1}
Optional gas	5.5% (v/v in carrier gas)
Integration time per isotope	0.1 s
Isotopes measured	^{117}Sn,^{118}Sn,^{119}Sn,^{120}Sn
Tune gas	100 ppm Xe in Ar
Total acquisition time	814 s
GC	***Agilent 6890***
Injection volume	2 µL
Mode	Splitless
Gas	He
Inlet temperature	240°C
Column flow	1 mL min^{-1}
Transfer line temperature	280°C

Calculation of the OTC concentrations was done by the standard addition calibration method and by the reverse ID-GC-ICPMS procedure, as described in detail by Rodríguez-González and coworkers (2005; 2013).

For the determination of OTCs in landfill leachates, the procedure of Vahčič et al. (2011a) was used. A liquid–liquid extraction procedure was used prior to the determination of OTCs in landfill leachate samples by GC-ICPMS. Briefly, 200 mL aliquots of landfill leachate samples were transferred into 500 mL dark glass reactor vessels along with methanol that was added in a concentration of 5 % relative to the sample volume. Mixtures were mechanically shaken for 2 h. After the shaking, 190 mL of a 0.2 mol L^{-1} Tris–citrate buffer was added to each sample, so that the total volume (sample, methanol plus buffer) was 400 mL.

A Tris–citrate buffer was prepared from Tris and citric acid to match a pH of 6 for derivatization. The pH was adjusted with citric acid or ammonia. Addition of a TPrT internal standard solution (200 ng L^{-1} Sn) followed. For the standard addition calibration method, mixtures of methyl- and butyltins were added to sample aliquots in concentrations ranging from 0 to 1000 ng L^{-1} Sn.

For the derivatization, 2 mL of 2 % (m/V) $NaBEt_4$ was added to the sample extracts, followed by the addition of 2 mL of hexane, as an extraction agent for the ethylated OTCs species. Samples were then mechanically shaken for 16 h. After that, the organic phase was collected into 15mL dark glass vials using a Pasteur pipette. The organic phase contained a dispersed emulsion. To separate the emulsion from the organic phase, 1 mL of 25 % KOH in methanol was added. The mixture was shaken for 5 min and centrifuged for 20 min at 4200×g. The clear organic phase was transferred into a dark glass vial. The concentrations of OTCs in the organic phase were determined by GC-ICPMS, using the standard addition method. The applied instrumental parameters were the same as described above. The procedure was also successfully applied to analyse OTCs in leachate aliquots of 10 and 50 mL.

All the analyses were made in duplicates.

4.3.3 Cleaning procedure

To avoid contamination all glassware were rinsed three times with tap water, soaked in 20 % nitric acid for at least 48 hours, rinsed three times with deionized water and heated at 400 °C for 4 hours.

4.3.4 Preparation of iron nanoparticles dispersions

For the efficient dispersion of FeNPs (nZVI, FeONPs or Fe_3O_4NPs), 30 mL of TMAH (25 wt % in methanol) was added to 0.75 g of FeNPs. The suspension was sonicated for 10 min, shaken for 1 h, and the FeNPs were removed with a magnet (Guardia et al., 2010). The FeNPs treated with TMAH were then added to 500 mL of the aqueous samples. Alternatively, the FeNPs were added to the samples and dispersed by mixing for 15 min. The amount of FeNPs added to an aqueous sample corresponded to a concentration of 1.5 g L^{-1} Fe.

4.3.5 Analytical procedure for the determination of element concentrations in environmental water samples by ICPMS

The concentrations of the elements in untreated Milli Q water, forest spring water and landfill leachate, before and after the FeNPs treatment, were determined by ICPMS under optimised measurement conditions and are presented in Table 3.

Table 3: ICPMS operating parameters for the determination of element concentrations.

Parameter	Type/Value	He mode (4.5 mL He min^{-1})	No gas mode
Sample introduction			
Nebuliser	Miramist		
Spray chamber	Scott		
Skimmer and sampler	Ni		
Plasma conditions			
Forward power	1550 W		
Plasma gas flow	15.0 L min^{-1}		
Carrier gas flow		1.00 L min^{-1}	1.00 L min^{-1}
Make-up gas flow		0.15 L min^{-1}	0.15 L min^{-1}
QP bias		-15.0 V	-3.0 V
Oct bias		-18.0 V	-8.0 V
Cell entrance		-40.0 V	-30.0 V
Cell exit		-60 V	-50 V
Deflect		0 V	12.8 V
Plate bias		-60 V	-40 V
Sample uptake rate	0.3 mL min^{-1}		
Data acquisition parameters			
Isotopes monitored		^{27}Al, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{78}Se, ^{88}Sr, ^{95}Mo	^{111}Cd, ^{118}Sn, ^{121}Sb, ^{137}Ba, ^{208}Pb
Isotopes of internal standards		^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In	^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In

4.4 EXPERIMENTAL PROCEDURES

4.4.1 Procedure for the synthesis of ^{117}Sn-enriched tributyltin

The synthesis was performed in a 10 mL Teflon vial. 10 mg of a ^{117}Sn metallic plate (0.085 mmol) was suspended in 1 mL of anhydrous diethylether and cooled in an ice bath. Bromine (40 mg, 0.250 mmol) was slowly added to the suspension and the solution was stirred for 30 min in the ice bath.

In the second step that followed immediately after the bromination, 0.50 mL of a 2.5 mol L^{-1} solution of butyllithium (1.25 mmol) was added slowly under an argon atmosphere and left to stir in the ice bath for an hour.

In the clean-up phase that followed, water (1 mL) was slowly added to the reaction mixture, followed by addition of 4 mL of diethyl ether. The mixture was capped and shaken. After separation, the organic phase was transferred (Pasteur pipette) to a 25 mL round-bottomed flask. The remaining aqueous phase from the glass vial was washed three times with fresh 4 mL portions of diethylether and the organic phases combined in the round-bottomed flask. The residual traces of water in the organic phase were removed by the addition of anhydrous sodium sulphate. The organic phase was then filtered through cotton wool into a glass tube that fitted into a controlled temperature system. To ensure the quantitative transfer of the organic phase, the cotton wool and bottle walls were washed several times with small portions of diethylether and these contents were also added to the glass tube. Diethyl ether was then evaporated at 30 °C under a gentle stream of nitrogen.

In the last step 1 mL of acetonitrile and 26 μL of 37 % HCl were added to the TeBT product and the contents were stirred for 4 h in the dark at a controlled temperature of 50 ± 0.1 ºC.

To remove HCl, 5 mL of water and 10 mL of dichloromethane were added and the contents transferred to a separation funnel. The organic phase was collected and the aqueous phase was washed twice with 10 mL of dichloromethane. Traces of water were then removed by anhydrous sodium sulphate and the solvent removed under reduced pressure. The ^{117}TBTCl was stored in 10 mL of methanol in an amber vial at 4 ºC.

The reactions were performed in a fume cupboard. The necessary time to complete the procedure was about 7 h.

Caution: Although we have encountered no difficulties, routine precautions (shields, fume hoods, avoidance of metals and their salts) should be observed whenever possible, as bromine and OTCs are potentially hazardous for health.

4.4.2 Experimental set-up to follow the transformation of organotin compounds in landfill leachate

First Sn-enriched spikes were prepared. $SnCl_4$ was prepared by adding 1 mL of *aqua regia* to 10 mg of an enriched ^{117}Sn-enriched metal plate. $SnCl_2$ was prepared by adding 1 mL of concentrated HCl to 10 mg of an enriched ^{117}Sn-enriched metal plate and warm it to 160 °C on a hot plate. The synthesis of ^{117}TBTCl was performed via the procedure described in paragraph 4.4.1. The in-house synthesis of ^{119}DBTCl started from a ^{119}Sn-enriched metal plate. The synthesis process, reported by Ugo et al., (1987) was adapted towards the use of a 10 mg ^{119}Sn-enriched metal plate as starting material. The reaction mixture was stored at 4 °C in the dark in 10 mL of methanol.

The experimental set-up consisted of six duplicate 3 L amber bottles, which were filled with 2 L of landfill leachate sample. Ten of them were spiked with a Sn-enriched OTC or an ionic Sn-enriched standard. Spiking was performed with $^{117}SnCl_{2,}$ $^{117}SnCl_{4,}$ ^{117}Sn-enriched TBT, ^{119}Sn-enriched DBT or a ^{119}Sn-enriched butyltin mix. Since the sum of the concentrations of methytin and butyltin compounds in the landfill leachate from Barje ranged between 500 and 1000 ng Sn L^{-1} (Vahčič et al., 2011a), the Sn-enriched standards were added in a concentration of approximately 1000 ng Sn L^{-1}. These concentrations were supposed to be non-toxic to the bacterial community in the leachate and enabled the investigation of the transformation processes. Two control bottles were left unspiked. All bottles were tightly closed with aluminium covered caps, shaken to get homogeneous samples and/or equilibration of spikes, and held at conditions, which are similar to those on the active landfill basin. The transformations of naturally present OTCs along with the Sn-enriched OTCs spikes in the leachates were followed over a time span of six months.

All experiments were carried out in duplicate.

4.4.3 Experimental set-up to follow the adsorption and degradation processes of tributyltin and trimethyltin in landfill leachates, treated with iron nanoparticles

400 mL aliquots of landfill leachate were transferred to 500 mL amber glass bottles and spiked with TBT or TMeT (1000 ng L^{-1} Sn). The bottles were capped with glass stoppers and the samples were shaken for 48 hours to allow equilibration of spiked TBT or TMeT. A 60 mL sample portion was used for OTCs analyses, while the other 60 mL portions were transferred to 250 mL amber glass bottles and treated with FeNPs at pH 8 (the pH of the spiked leachate), or the pH of the leachate was first adjusted to 3 with citric acid (1.5 g of citric acid per 60 mL of leachate) and then treated with dispersed FeNPs (iron load 1.5 g L^{-1}). The bottles were capped with glass stoppers and the samples were shaken for 3 to 7 days. In the leachates treated at pH 8, the iron precipitate was collected by a magnet, allowing its quantitative removal (more than 99 %) by decanting the clear leachate solution into another beaker. Before the untreated leachates and the leachates treated with FeNPs were analysed, a sequential filtration of the samples through 5000 nm, 450 nm and 2.5 nm filters was applied. 10 mL leachate fractions with particle sizes > 5000 nm, 450 - 5000 nm, 2.5 nm - 450 nm, < 2.5 nm were transferred to 30 mL amber glass vials and the concentrations of OTCs were determined by GC-ICPMS.

All experiments were carried out in duplicate.

4.4.4 Experimental set-up to follow the fate of various iron nanoparticles in aqueous matrices after the treatment

500 mL aliquots of aqueous samples were transferred into 1 L amber glass bottles. nZVI, FeONPs or Fe_3O_4NPs were added, using TMAH or mixing for dispersion, as described under 4.3.4. The treatment with FeNPs was performed by shaking the samples for 24 h. 60 mL sample aliquots were then taken in different time intervals: 15 min, 1 h, 4 h and 24 h after the FeNPs treatment, to follow the particle settlement. Sequential filtration of the samples through 5000 nm, 450 nm, 200 nm, 100 nm and 2.5 nm filters was applied. Accordingly, the concentrations of Fe and selected elements were determined, in 10 mL sample fractions with particle sizes 450 - 5000 nm, 200 - 450 nm, 100 - 200 nm, 2.5 nm - 100 nm and < 2.5 nm, by ICPMS. The same

procedure of sequential filtration and the determination of elements was also performed in untreated aqueous samples.

All experiments were carried out in duplicate.

5 RESULTS AND DISCUSSION

This chapter is based on the data of two published articles and two submitted manuscripts.

- Peeters Kelly, Iskra Jernej, Zuliani Tea, Ščančar Janez, Milačič Radmila. The micro-scale synthesis of ^{117}Sn-enriched tributyltin chloride and its characterization by GC-ICP-MS and NMR techniques. Chemosphere, 2014, 107, 386-392.
- Peeters Kelly, Zuliani Tea, Ščančar Janez, Milačič Radmila. The use of isotopically enriched tin tracers to follow the transformation of organotin compounds in landfill leachate. Water Research, 2014, 53, 297-309.
- Peeters Kelly, Lespes Gaëtane, Ščančar Janez, Milačič Radmila. Adsorption and degradation processes of tributyltin and trimethyltin in landfill leachates treated with iron nanoparticles. Water Research, 2015, submitted.
- Peeters Kelly, Lespes Gaëtane, Zuliani Tea, Ščančar Janez, Milačič Radmila. The fate of iron nanoparticles in environmental waters treated with nanoscale zerovalent iron, FeO and Fe_3O_4. Water Research, 2015, manuscript prepared.

5.1 MICRO-SCALE SYNTHESIS OF ^{117}Sn-ENRICHED TRIBUTYLTIN CHLORIDE AND ITS CHARACTERIZATION BY GC-ICPMS AND NMR TECHNIQUES

5.1.1 Development of the procedure for synthesis of tributyltin chloride

5.1.1.1 Formation of $SnBr_4$ from Sn metal

Due to the high cost of ^{117}Sn enriched metal for the synthesis of isotopically enriched TBT, the development of the synthetic procedure was performed using metallic Sn powder with a natural isotopic abundance. Experiments were performed to produce TBT via a simple synthetic path, starting from 10 mg of Sn metal. In the first step of the synthesis, ionic Sn(IV) species should be formed. The formation of Sn(IV) chloride ($SnCl_4$) was avoided because it is a volatile, air-, light-, and moisture sensitive compound. The formation of Sn(IV) iodide

(SnI_4) was also not desirable due to product losses during the clean-up procedure. Therefore, the Sn powder was brominated to form Sn(IV) bromide ($SnBr_4$).

$$Sn + 2Br_2 \rightarrow SnBr_4 \qquad [7]$$

The synthesis was performed in a 10 mL vial. The bromination was carried out in an ice bath. A temperature close to 0 ºC prevents melting of the formed crystalline $SnBr_4$, hence minimising hydrolysis processes. This precaution is critical to get an optimal synthesis yield.

To examine the parameters that influence the extent of adsorption of $SnBr_4$ on the vial walls, parallel experiments were carried out in glass and Teflon. The data revealed that the synthesis yield was about 50 % in glass and 60 % in Teflon vials. So, it was concluded that the adsorption of the formed ionic Sn species is lower on the surface of Teflon. Therefore Teflon vials were used in further experiments in the first and the second synthesis steps.

5.1.1.2 Formation of tetrabutyltin from $SnBr_4$

In the second step that followed immediately after bromination, BuLi was added under an argon atmosphere in an ice bath. The usage of tri-*n*-butyltin-lithium for butylation of $SnCl_2$ was reported almost 60 years ago by Gilman and Rosenberg (1953). The BuLi, used in our experiment is commercially available and is easier to purify than Grignard-based reagents, which require several purification steps (Sutton et al., 2000).

$$SnBr_4 + 4BuLi \rightarrow SnBu_4 + 4LiBr \qquad [8]$$

After butylation the aqueous phase was removed by phase separation. Clean-up was performed by several washings with diethylether and the addition of anhydrous sodium sulphate as described under 4.4.1. The organic phase was then filtered through cotton wool into a glass tube that fitted into a controlled temperature system, and diethylether was evaporated.

5.1.1.3 Optimisation of the parameters for preparation of tributyltin chloride from tetrabutyltin

In the last step, chlorination of TeBT was performed by the addition of HCl and the use of acetonitrile as solvent, to obtain TBTCl.

$$SnBu_4 + HCl \rightarrow SnBu_3Cl + BuH \qquad [9]$$

The experimental data proved that the synthetic procedure is only selective when controlled temperature conditions (deviation not more than ± 0.1 ºC) are assured.

Commercially available TeBT (100 mg) was dissolved in 1 mL of acetonitrile and 10 equivalents of 37 % HCl were added. The reaction mixture was stirred at 50 or 80 °C and the conversion of the crude reaction product was followed by NMR analysis, as this is a much faster technique than GC-ICPMS. The reaction was first performed at 80 °C and the influence of the reaction time was checked for 1, 2, 4 and 8 h. It was found experimentally that the reaction was fast and complete within 1 h. This rapid reaction does not allow conditions to be well controlled, while in further chlorination, degradation of TBT could occur. So, the reaction temperature was lowered to 50 °C and the same reaction times were applied. The data showed that for reaction times shorter than 2 h, TeBT did not react completely. With a reaction time of 4 h, TeBT was completely converted and only TBT was detected. On applying longer reactions times the possibility of degradation to DBT would be more likely to occur. The NMR spectra of the standard solutions of TeBT and TBTCl as well as the product obtained by reaction of TeBT with HCl at 50 °C for 4 h, are presented in Figure 6.

As may be seen from Figure 6C, no starting TeBT (Figure 6A) could be detected in the NMR spectrum, while the signals of the product are identical with the reference spectra of TBTCl (Figure 6B). Due to selective and quantitative chlorination of TeBT into TBT, there is no need for purification of TBT by fluorination of TBT chloride, precipitation of TBT fluoride and its chlorination back to TBT chloride as reported in the literature (Inagaki et al., 2007; Zuliani et al., 2012; Ruiz Encinar et al., 2000; Sutton et al., 2000)

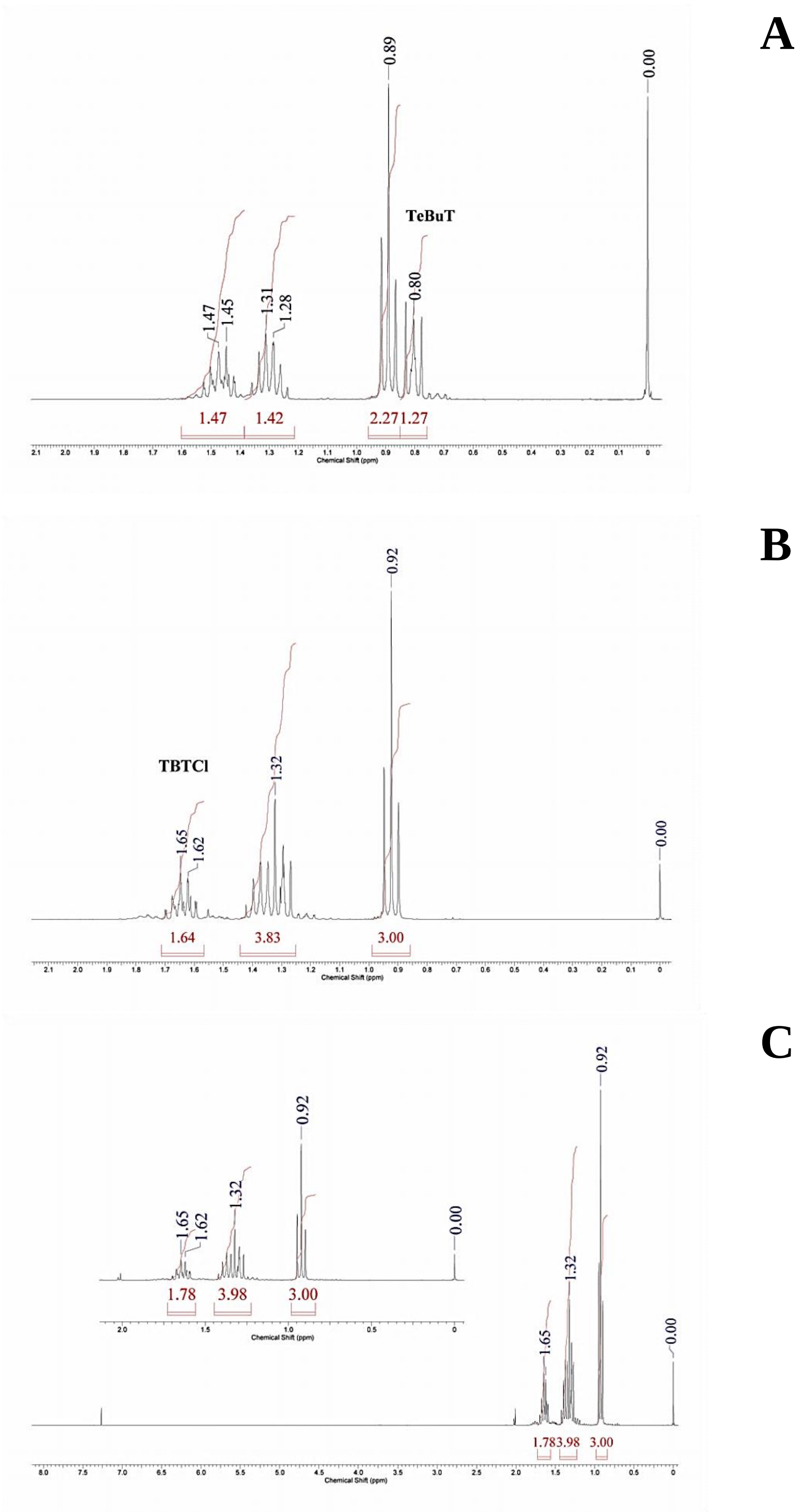

Figure 6: NMR spectra of A: the standard solution of TeBT, B: the standard solution of TBTCl and C: the product obtained by the reaction of TeBT with HCl at 50 °C for a reaction time of 4 h.

The overall synthetic procedure was then applied on a micro-scale level, starting from 10 mg of metallic Sn powder and conducting the reaction of TeBT with HCl at 50 °C for different reaction times. The product was characterised by the use of the more sensitive GC-ICPMS technique, which also enabled the quantification of TBT and side products. The results of these experiments are presented in Figure 7.

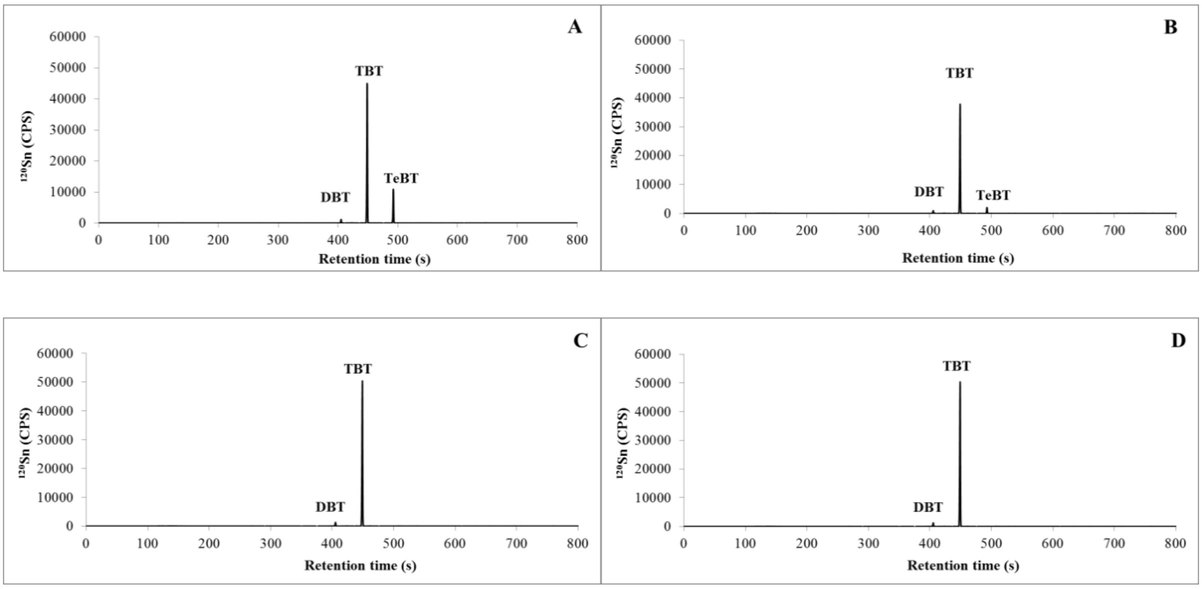

Figure 7: GC-ICPMS chromatograms of the products obtained after the synthesis of TBTCl from 10 mg of metallic Sn powder, conducting the reaction of TeBT with HCl at 50 °C for different reaction times. A: 1 h, B: 2 h, C: 4 h, D: 6 h.

As in the experiments based on the characterisation of the products with NMR (after the reaction of TeBT with HCl), the data of Figure 6 confirmed that the overall synthetic procedure gave a TBT product of high purity for reaction times between 4 and 6 h. From the chromatograms of Figure 6 it was evident that at reaction times shorter than 2 h, TeBT did not completely react. On the basis of these results, the reaction of TeBT with HCl at 50 °C for a reaction time of 4 h was found to be optimal.

5.1.2 Preparation of ^{117}Sn-enriched tributyltin chloride and natural abundance tributyltin chloride, and their characterization by speciation analysis, using GC-ICPMS

Under the described micro-scale synthesis protocol, the procedure was applied to prepare ^{117}Sn-enriched TBTCl from ^{117}Sn-enriched metal (4.4.1).

To check whether there was any difference in the selectivity and efficiency of the synthesis between the procedures starting from 10 mg of ^{117}Sn-enriched metallic plate or natural abundance Sn powder, the synthesis was carried out in parallel experiments. The composition of the synthesized ^{117}Sn-enriched TBTCl and natural abundance TBTCl was characterised by speciation analysis using GC-ICPMS. The results are presented in Figure 8.

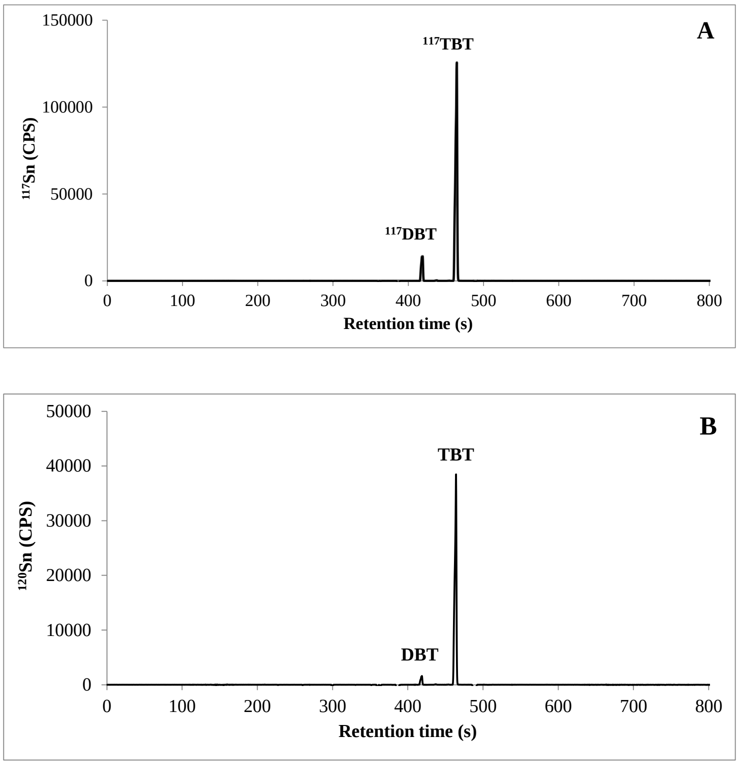

Figure 8: Composition of the products of the synthesis. A: ^{117}Sn-enriched TBT and B: natural abundance TBT. Speciation analysis was performed by GC-ICPMS.

From the data shown in Figure 8, it is evident that ^{117}TBT and TBT are the major species present in the chromatograms A and B, respectively. Only a small peak of ^{117}DBT in chromatogram A and traces of DBT can be observed in chromatogram B. The degree of degradation of ^{117}TBT is negligibly higher than for natural abundance TBT. The different signal intensities in chromatograms A and B are related to the different abundances of the recorded isotopes.

5.1.3 Quantification of ^{117}Sn-enriched tributyltin and natural abundance tributyltin, and the yields of the synthesis

The quantification of the synthesized ^{117}Sn-enriched TBT and natural abundance TBT, as well as their by-products, was done by calculation of their concentrations using the standard addition calibration method, and by the reverse ID-GC-ICPMS technique. These results and the synthesis yields are presented in Table 4.

Table 4: Quantification of synthesised ^{117}Sn-enriched TBT and natural abundance TBT by the standard addition calibration method and the reverse ID-GC-ICPMS technique. The synthesis yield is also presented.

Species synthesized	Standard addition calibration method	Reverse ID-ICPMS	Synthesis yield
	(mg Sn)	(mg Sn)	(%)
^{117}Sn-enriched TBT	6.127 ± 0.306	6.125 ± 0.02	63.2 ± 0.9
^{117}Sn-enriched DBT	0.431 ± 0.02	/	
TBT	5.997 ± 0.29	/	60.0 ± 1.0
DBT	0.203 ± 0.01	/	

/non applicable

The data of Table 4 demonstrate that the agreement between the results for ^{117}Sn-enriched TBT concentrations obtained by the standard addition calibration method and by the reverse ID-GC-ICPMS technique was better than 0.1 %. The purity of ^{117}TBT was 93.5 %, while the remaining 6.5 % corresponds to ^{117}DBT. The purity of synthesised natural abundance TBT was comparable to that of commercially available TBT containing only 3.2 % of DBT.

After careful optimisation of all steps of synthesis, high yields were obtained. Considering the isotopic enrichment (97 %), the starting amount for ^{117}Sn-enriched metallic plate was 9.7 mg and 10 mg for natural abundance Sn powder. So, the synthesis yields for ^{117}Sn-enriched TBTCl and natural abundance TBTCl were found to be 63.2 and 60.0 %, respectively. These results indicate that there was no significant difference in selectivity and efficiency between the synthesised ^{117}Sn-enriched TBT and natural abundance TBT. It was experimentally confirmed that the developed procedure is applicable for the synthesis of ^{117}Sn-enriched TBTCl, which may be used as a tracer in the investigation of the fate of OTCs in the environment and as a spike for the accurate determination of TBT concentrations in environmental samples by isotope dilution mass spectrometry.

5.1.4 Stability of the product and the reproducibility of the synthesis

An important characteristic of any newly synthesized compound is its stability under the applied storage conditions (methanol, 4 ºC, dark). A stability test was performed on ^{117}Sn-enriched TBT and natural abundance TBT by monitoring their concentrations over six months using GC-ICPMS. The quantification of ^{117}Sn-enriched TBT was performed by reverse ID-ICPMS and for natural abundance TBT by the standard addition calibration method. The results are presented in Figure 9.

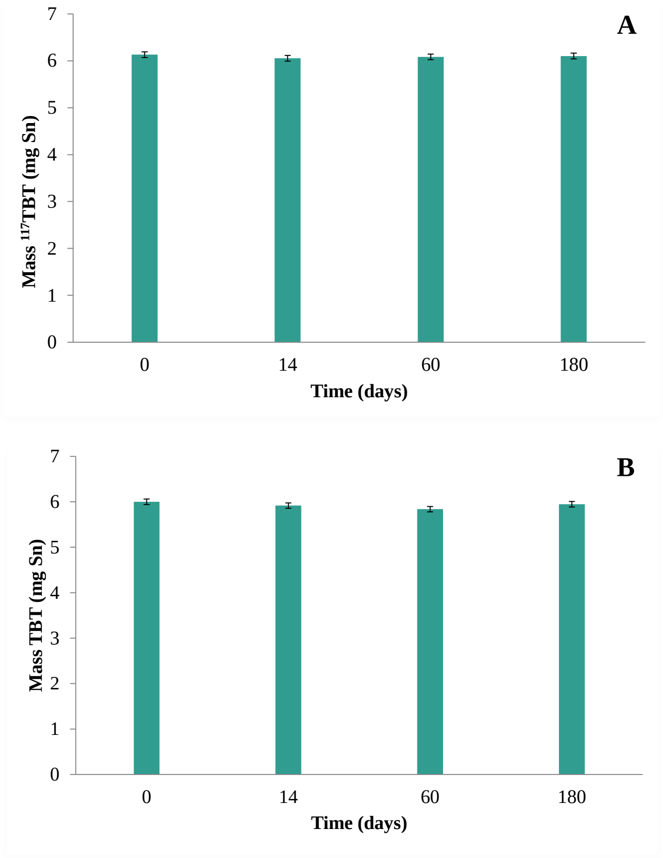

Figure 9: Stability of A: ^{117}Sn-enriched TBT and B: natural abundance TBT over time.

From the data in Figure 9 it can be seen that the synthesized ^{117}Sn-enriched TBT and natural abundance TBT are stable for at least six months. Deviations in the concentrations determined did not exceed ± 2 %. The stability of TBT species will be followed in the future to obtain data for a longer time period.

In a view of the high costs for the preparation of ^{117}Sn-enriched TBT, the reproducibility of the procedure developed was verified by seven independent syntheses of natural abundance TBT. Characterization and quantification of the products was performed by GC-ICPMS. The data showed that the purity of synthesised TBT ranged between 96 and 98 %, while the reproducibility of the yield was 60.0 ± 5 %.

The reported literature procedures for the preparation of TBT on a small-scale, starting from 0.5 to 1.4 g of Sn powder (Sutton et al., 2000) were not applicable to the micro-scale level. The advantage of the procedure developed over those previously reported is its ability to synthesise TBT efficiently on a micro-scale level, which is of crucial importance due to the high costs of Sn-enriched metal. Other advantages are the simplicity, high synthesis yield and repeatability of the procedure, and the stability of the synthesised ^{117}TBTCl.

5.2 THE USE OF ISOTOPICALLY ENRICHED TIN TRACERS TO FOLLOW THE TRANSFORMATION OF ORGANOTIN COMPOUNDS IN LANDFILL LEACHATE

The prevailing OTCs in landfill leachates are methyltin and butyltin compounds (Pinel-Raffaitin et al., 2007, Pinel-Raffaitin et al., 2008; Vahčič et al., 2011a). Municipal landfills exhale also volatile methyltin, ethyltin and mixed ethylmethyltin compounds (Pinel-Raffaitin et al., 2008; Mitra et al., 2005; Michalzik et al., 2007). The mechanisms of degradation and methylation of OTCs were most frequently studied in the marine environment (Hoch, 2001; Rosenberg, 2005; de Carvalho Oliveira and Santelli, 2010). The degradation rates of OTCs under different environmental conditions may be influenced by their exposure to ultraviolet irradiation (Craig et al., 2003) or through biodegradation by various microalgae and bacteria (Dubey and Roy, 2003; Stasinakis et al., 2005; Kawai et al., 1998). Beside the antropogenic sources, methyltin compounds can be formed by biomethylation processes (Rosenberg, 2005; Craig and Rapsomanikis, 1985; Rapsomanikis and Weber, 1985; Ashby and Craig, 1988, 1991; Ridley et al., 1977; Thayer, 2002). CH_3B_{12}, the methyl coenzyme of vitamin B_{12}, which is produced from bacteria, is able to methylate tin (Ridley et al., 1977; Chen et al., 2007). Laboratory studies confirmed that in seawater-sediment mixtures butyltins were methylated, producing mixed methyltributyl compounds (Vella and Adami, 2001). Pinel-Raffaitin et al. (2008) investigated the occurrence of OTCs in landfill leachates and landfill gases and proposed their possible transformations. To better understand the pathways and mechanisms of OTC transformation in leachates, in the present doctoral thesis the degradation and/or formation of OTCs was investigated by the use of Sn-enriched tracers as described under 4.4.1, (Peeters et al., 2014a) and 4.4.2. Transformation of OTCs in spiked leachates were followed at *m/z* of the enriched isotope of the Sn-enriched spikes and at *m/z* 120, which allowed to simultaneously observe the processes of OTCs in the leachate itself and of the added spike. In parallel, the transformation processes were monitored also in a non-spiked leachate sample at *m/z* 120.

5.2.1 Occurrence of organotin compounds in landfill leachates and accuracy check

First, the concentrations of OTCs in the leachate, at the start of the experiment, were determined. They were found to be 200 ± 20 ng Sn L^{-1} for TMeT, 95 ± 10 ng Sn L^{-1} for DMeT, 40 ± 4 ng Sn L^{-1} for MMeT and 15 ± 2 ng Sn L^{-1} for TBT, 40 ± 4 ng Sn L^{-1} for DBT and 30 ± 5 ng Sn L^{-1} for MBT, respectively. The concentration of total Sn in the leachate was determined by ICPMS after microwave assisted digestion (Vahčič et al., 2011a) and was found to be 80 ± 5 μg Sn L^{-1}. The total iron concentration was 865 ± 30 μg L^{-1} and total manganese content 160 ± 2 μg L^{-1}.

Since there is no certified reference material for landfill leachates available, a spike recovery test was used for the accuracy check. For this purpose landfill leachate was spiked with butyltin and methyltin compounds. The results are presented in Table 5.

Table 5: Recoveries for OTCs in landfill leachate spiked with butyltin and methyltin compounds. The concentrations of OTCs were determined by the GC-ICPMS procedure using the standard addition calibration method. The Sn signal was monitored at *m/z* 120.

OTC	Concentration of OTC in leachate (ng Sn L^{-1})	Concentration of OTC added (ng Sn L^{-1})	Concentration of OTC found (ng Sn L^{-1})	Recovery (%)
TBT	9.5 ± 0.8	20.0 ± 0.2	28.3 ± 2.2	96
DBT	8.2 ± 0.6	20.0 ± 0.2	28.8 ± 2.3	102
MBT	101± 8	100 ± 1	179 ± 15	89
TMeT	210 ± 15	200 ± 2	416 ± 30	102
DMeT	150 ± 10	200 ± 2	350 ± 25	100
MMeT	88 ± 7	100 ± 1	175 ± 15	93

± represents deviation from the mean value of two replicates

Recoveries of the spiked target compounds in the samples ranged from 89 % to 102 % for butlytins and from 93 % to 102 % for methyltins. From the results of the recovery tests, it is evident that the applied analytical procedure was suitable for its intended use to follow the transformation of OTCs in landfill leachates.

5.2.2 Transformation of organotin compounds in leachates spiked with ^{117}Sn-enriched $SnCl_2$ or $SnCl_4$

In aqueous solutions Sn^{2+} and Sn^{4+} have a strong tendency to hydrolyze. The reaction with water yields sparingly soluble tin hydroxides. The extent of hydrolysis is higher for Sn^{4+}, which is a strong Lewis acid, than for Sn^{2+}, which exhibits more basic properties (Graf, 1998). It can be expected that after the spiking of landfill leachates with ^{117}Sn-enriched $SnCl_2$ or $SnCl_4$, the concentrations of ionic $^{117}Sn^{2+}$ and $^{117}Sn^{4+}$ species in leachates will decrease due to the hydrolysis. The transformation processes of OTCs in leachates spiked with 1000 ng Sn L^{-1} of $^{117}SnCl_2$ and $^{117}SnCl_4$ and unspiked leachate samples, followed over a time span of six months are presented in Figures 9 and 10.

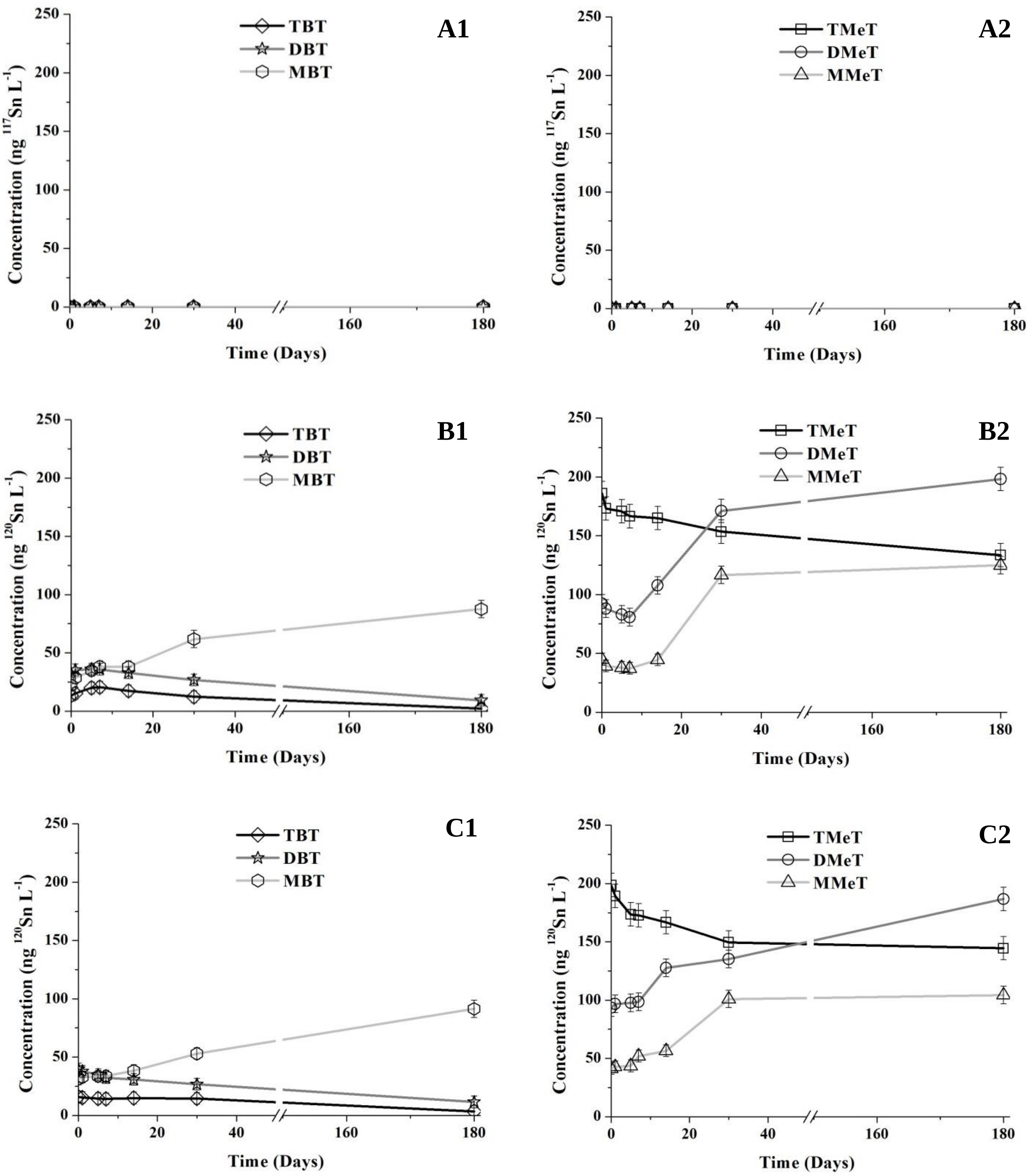

Figure 10: Transformation of OTCs in a landfill leachate over a time span of 6 months. The landfill leachate was spiked with ^{117}Sn-enriched $SnCl_2$ (1000 ng Sn L^{-1}) and the concentrations were determined at *m/z* 117 for (A1) butyltin compounds and (A2) methyltin compounds, as well as at *m/z* 120 for (B1) butyltin compounds and (B2) methyltin compounds. The concentrations of the OTCs in an unspiked leachate were also determined at *m/z* 120 for (C1) butyltin compounds and (C2) methyltin compounds.

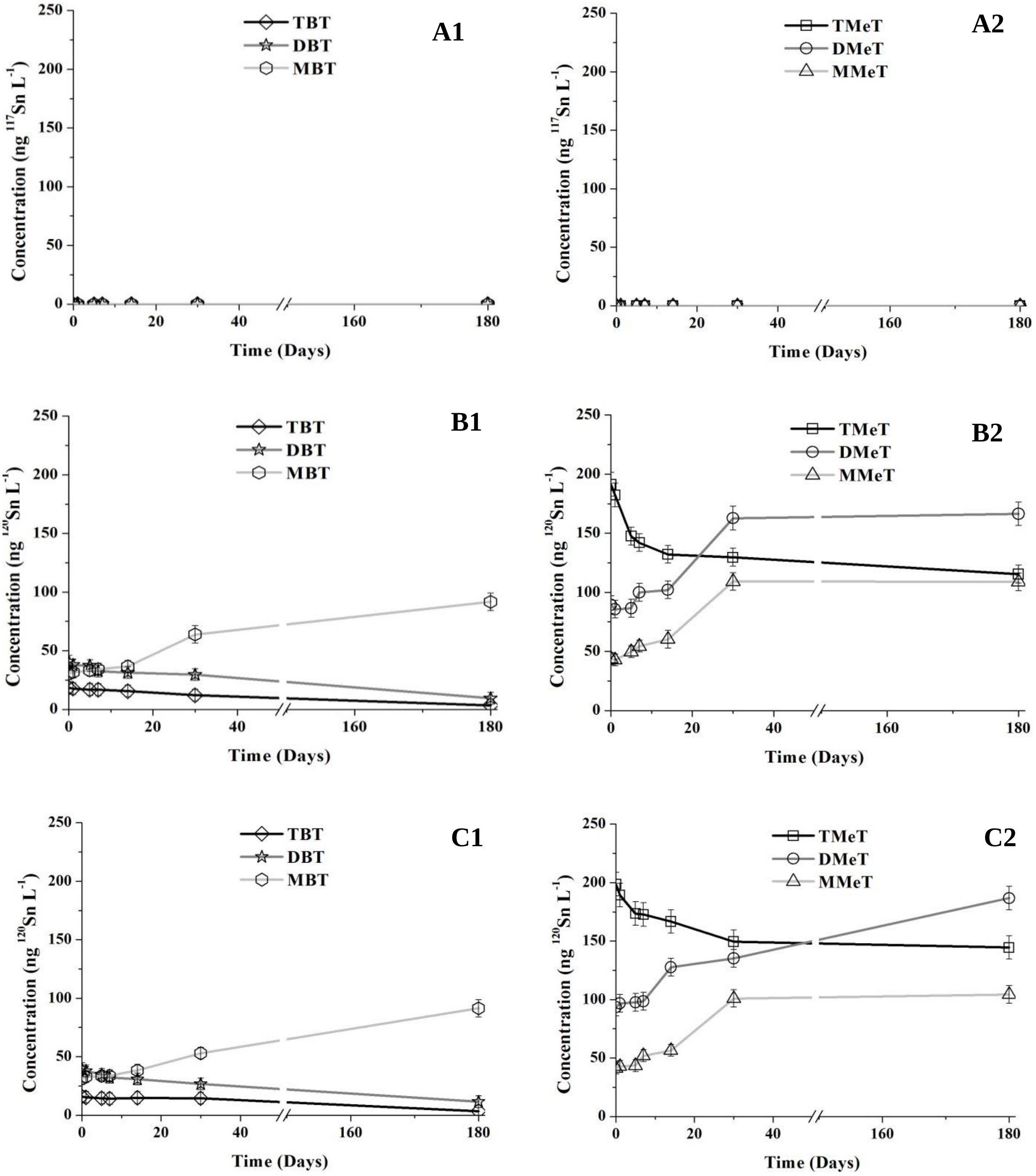

Figure 11: Transformation of OTCs in a landfill leachate over a time span of 6 months. The landfill leachate was spiked with ^{117}Sn-enriched SnCl$_4$ (1000 ng Sn L^{-1}) and the concentrations were determined at *m/z* 117 for (A1) butyltin compounds and (A2) methyltin compounds, as well as at *m/z* 120 for (B1) butyltin compounds and (B2) methyltin compounds. The concentrations of the OTCs in an unspiked leachate were also determined at *m/z* 120 for (C1) butyltin compounds and (C2) methyltin compounds.

As expected, ^{117}Sn-enriched butyltins were not formed from the added $^{117}SnCl_2$ and $^{117}SnCl_4$ (Figure 10A1 and Figure 11A1), but degradation of the initially present TBT and DBT, resulting in subsequent formation of MBT, can be observed by following their concentrations at *m/z* 120 in the spiked (Figure 10B1 and Figure 11B1) and unspiked leachates (Figure 10C1 and Figure 11C1).

The concentrations monitored at *m/z* 117 (Figure 9A2 and Figure 10A2) show that no ^{117}Sn-enriched methyltin species were formed. Nevertheless, the variations in the concentrations of the initially present methyltins in the leachate itself, followed at *m/z* 120, indicate that during the course of the experiment methylation processes were carried on in the spiked (Figure 10B2 and Figure 11B2) and unspiked leachate samples (Figure 10C2 and Figure 11C2). Similar trends of methylation in the spiked and unspiked samples show that the addition of inorganic ^{117}Sn-enriched spikes did not influence the processes in the leachate itself. From the data followed at *m/z* 120, it can be further seen that the concentration of MMeT was gradually increased within the first 30 days and remained then constant till the end of the experiment. The concentration of DMeT was progressively increased during the course of the experiment, while TMeT exhibited the tendency of degradation during the time span of the investigation. The latter observations indicate that there were favourable conditions for methylation processes in the leachate. Under environmental conditions, biomethylation of ionic tin species by CH_3B_{12} is most likely the main pathway of methyltin formation (Ridley et al., 1977; Rapsomanikis and Weber, 1985; Thayer, 2002; Rosenberg, 2005, Chen et al., 2007). Rapsomanikis and Weber (1985) reported the formation of MMeT from tin(II) by methylcobalamin in the presence of manganese dioxide. Ridley et al. (1977) proposed mechanisms of MMeT formation through the cleavage of CH_3B_{12} by a stanyl radical, $SnX_3^{\bullet}$ (X being a counter anion e.g. chloride). Successive alkylation of MMeT results in the formation of DMeT, TMeT and tetramethyltin (TeMeT) species. Chen and co-workers (2007) demonstrated that in aqueous solutions, the methyl group from CH_3B_{12} can be transferred to tin as a methyl radical, a carbonium or carbanion. The data also show the continuous formation/degradation of the initially present methyltin species during the course of the experiment (Figure 10B2, 10C2 and Figure 11B2, 11C2). The methylation processes of ionic Sn species in the leachate are most likely related to the transfer of the methyl group from CH_3B_{12}, according to the mechanisms proposed by Ridley et al. (1977) and Chen et al. (2007). The gradual increase in DMeT is a consequence of its formation from MMeT and degradation of TMeT. Stepwise alkylation of MMeT produces TeMeT which is a gaseous species, and so, it was not detected in the leachate. In the landfill, TeMeT is collected together with a CH_4 gas. In the gas pipes it is demethylated to TMeT, which is adsorbed and concentrated in condensed water. The condensate from the gas pipes, containing high concentrations of TMeT, is returned to the landfill leachate and contributes to the high concentration of methyltins in the leachate (Ilgen et al. 2008), as was observed also at the start of our experiment. When leachate samples were taken to the laboratory, the fresh input of TMeT from the condensate of gaspipes was interrupted and the concentration of TMeT was gradually decreased during the course of the experiment, since the rate of degradation was higher than the rate of TMeT formation from MMeT and DMeT.

The reason that it was not possible to observe methylation processes in leachates spiked with $^{117}Sn^{2+}$ and $^{117}Sn^{4+}$ (1000 ng Sn L^{-1}) (Figure 10A2 and 11A2) is most likely related to the hydrolysis, which produced insoluble tin precipitates as predominant tin species. So, higher concentrations of $^{117}Sn^{2+}$ and $^{117}Sn^{4+}$ (100 µg Sn L^{-1}), which were close to the total Sn concentrations found in the investigated landfill leachate and those reported in the literature (Pinel-Raffaitin et al., 2008), were added. The concentrations of methyltin species were then determined 3 and 10 days after spiking (Figure 12).

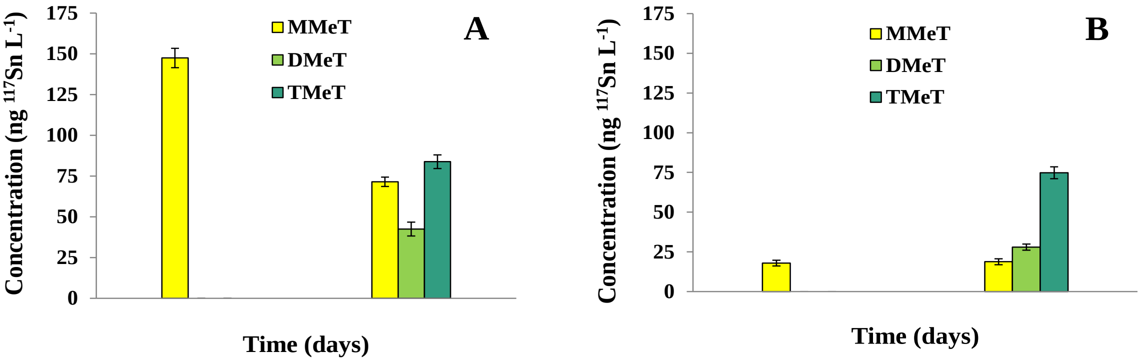

Figure 12: Transformation of methyltin compounds in a landfill leachate over a time span of 10 days. The landfill leachate was spiked with (A) 100 µg Sn L^{-1} of ^{117}Sn-enriched $SnCl_2$ or (B) 100 µg Sn L^{-1} of ^{117}Sn-enriched $SnCl_4$. The concentrations were determined at *m/z* 117.

As can be seen, after 3 days, only ^{117}MMeT was formed from both, $^{117}Sn^{2+}$ and $^{117}Sn^{4+}$. The extent of ^{117}MMeT formation was higher from $^{117}Sn^{2+}$, presumably due to its lower extent of hydrolysis. During a longer incubation time, ^{117}DMeT and ^{117}TMeT were also formed, most probably from ^{117}MMeT, which was the first observed methyltin species. The results of our experiments demonstrate that methylation processes in the leachate are carried out from both, Sn^{2+} and Sn^{4+}. As proposed by Ridley et al. (1977) it is possible that Sn^{2+} was oxidised to a stanyl radical by Fe(III) and Mn(IV), which were present in the leachate, while Sn^{4+} was reduced by the organic matter, also forming a stanyl radical. Homolytic cleavage of CH_3B_{12} by this stanyl radicals gave MMeT and by stepwise alkylation, also DMeT and TMeT species were formed. The transfer of the methyl group from CH_3B_{12} to tin was possible also as a carbonium or carbanion (Chen et al., 2007). Björn et al. (2011) studied the fate of methyltin under simulated landfill conditions over a period of 30 weeks. At the end of the experiment small amounts of MMeT were formed from 500 μg L^{-1} of $SnCl_4$ added to an inoculum of the municipal solid waste, while demethylation was observed when TMeT, DMeT and MMeT were added.

The data of our study demonstrated that the distribution of methyltin species in the leachate is governed by both, methylation and degradation processes, while hydrolysis of Sn^{2+} and Sn^{4+} species is a limiting factor, which controls the extent of methyltin formation.

5.2.3 Transformation of organotin compounds in leachates spiked with ^{117}Sn-enriched tributyltin, ^{119}Sn-enriched dibutyltin or a ^{119}Sn-enriched butyltin mix

The transformation processes of OTCs in leachates spiked with 920 ng Sn L^{-1} of ^{117}Sn-enriched TBT and 880 ng Sn L^{-1} of ^{119}Sn-enriched DBT, as well as a ^{119}Sn-enriched butyltin mix (815 ng Sn L^{-1} of TBT, 420 ng Sn L^{-1} of DBT and 60 ng Sn L^{-1} of MBT) and unspiked leachate samples, followed over a time span of six months, are presented in Figures 13 to 15.

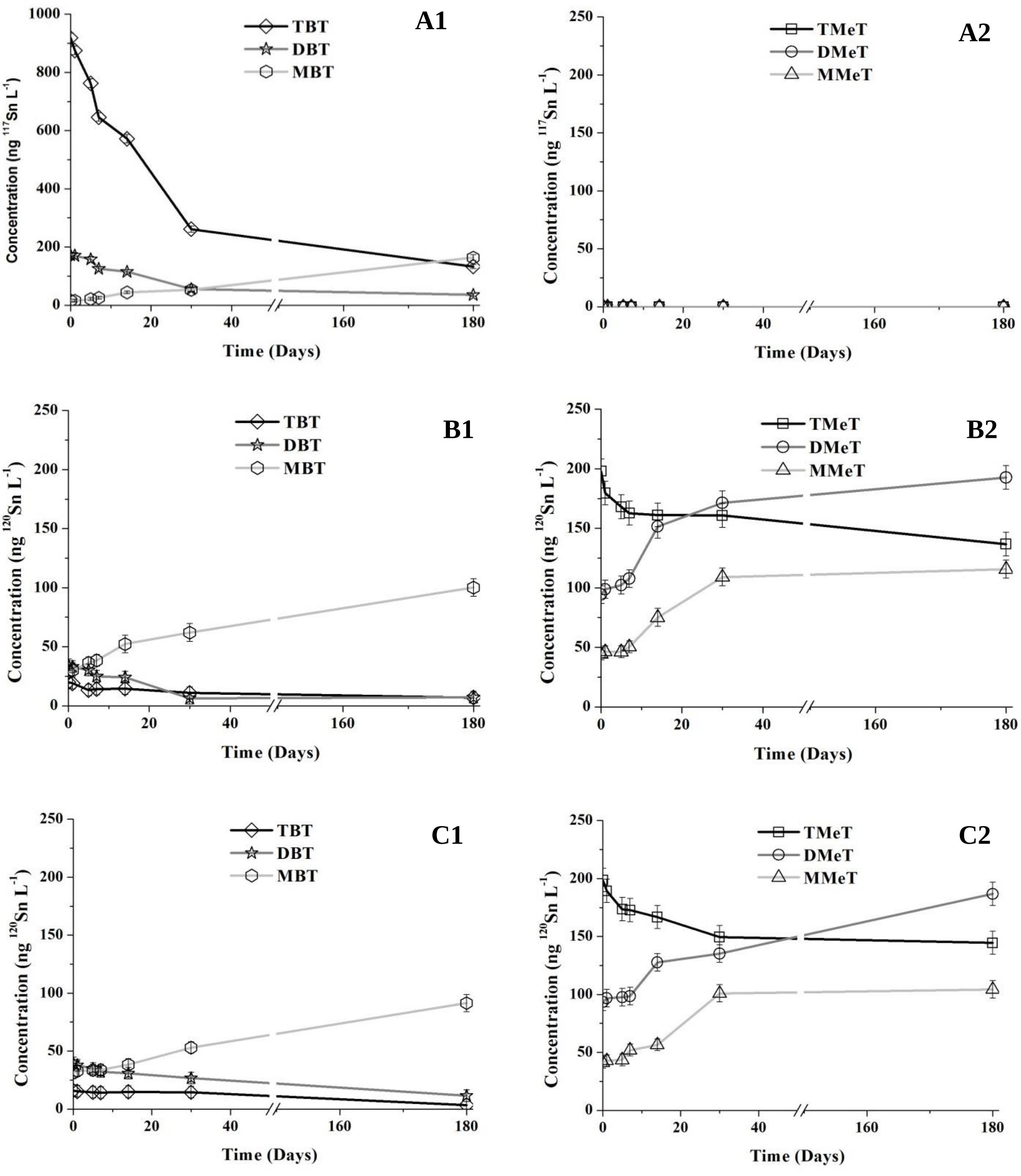

Figure 13: Transformation of OTCs in a landfill leachate over a time span of 6 months. The landfill leachate was spiked with ^{117}Sn-enriched TBT (920 ng Sn L^{-1}) and the concentrations were determined at *m/z* 117 for (A1) butyltin compounds and (A2) methyltin compounds, as well as at *m/z* 120 for (B1) butyltin compounds and (B2) methyltin compounds. The concentrations of the OTCs in an unspiked leachate were also determined at *m/z* 120 for (C1) butyltin compounds and (C2) methyltin compounds.

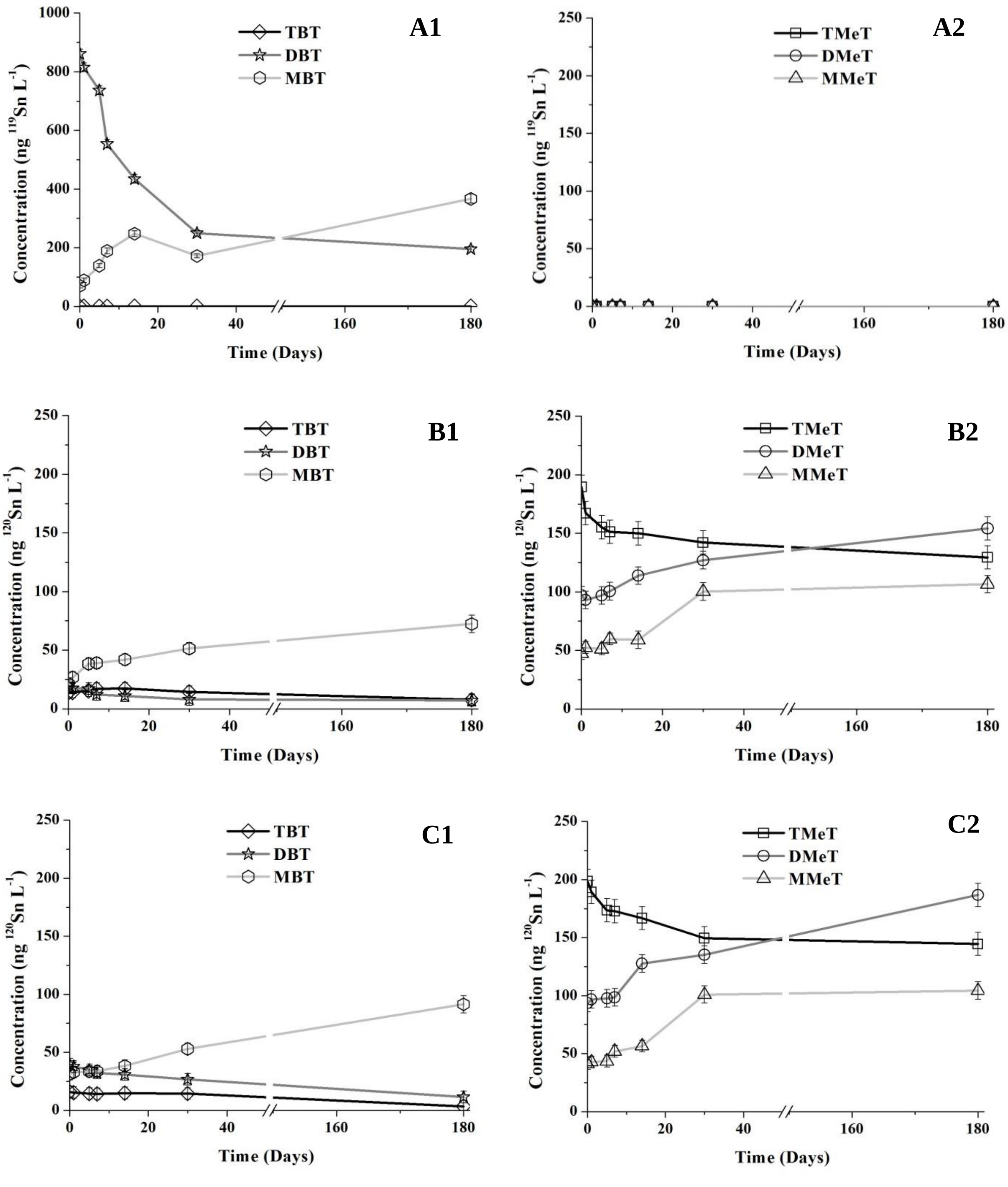

Figure 14: Transformation of OTCs in a landfill leachate over a time span of 6 months. The landfill leachate was spiked with ^{119}Sn-enriched DBT (880 ng Sn L^{-1}) and the concentrations were determined at *m/z* 119 for (A1) butyltin compounds and (A2) methyltin compounds, as well as at *m/z* 120 for (B1) butyltin compounds and (B2) methyltin compounds. The concentrations of the OTCs in an unspiked leachate were also determined at *m/z* 120 for (C1) butyltin compounds and (C2) methyltin compounds.

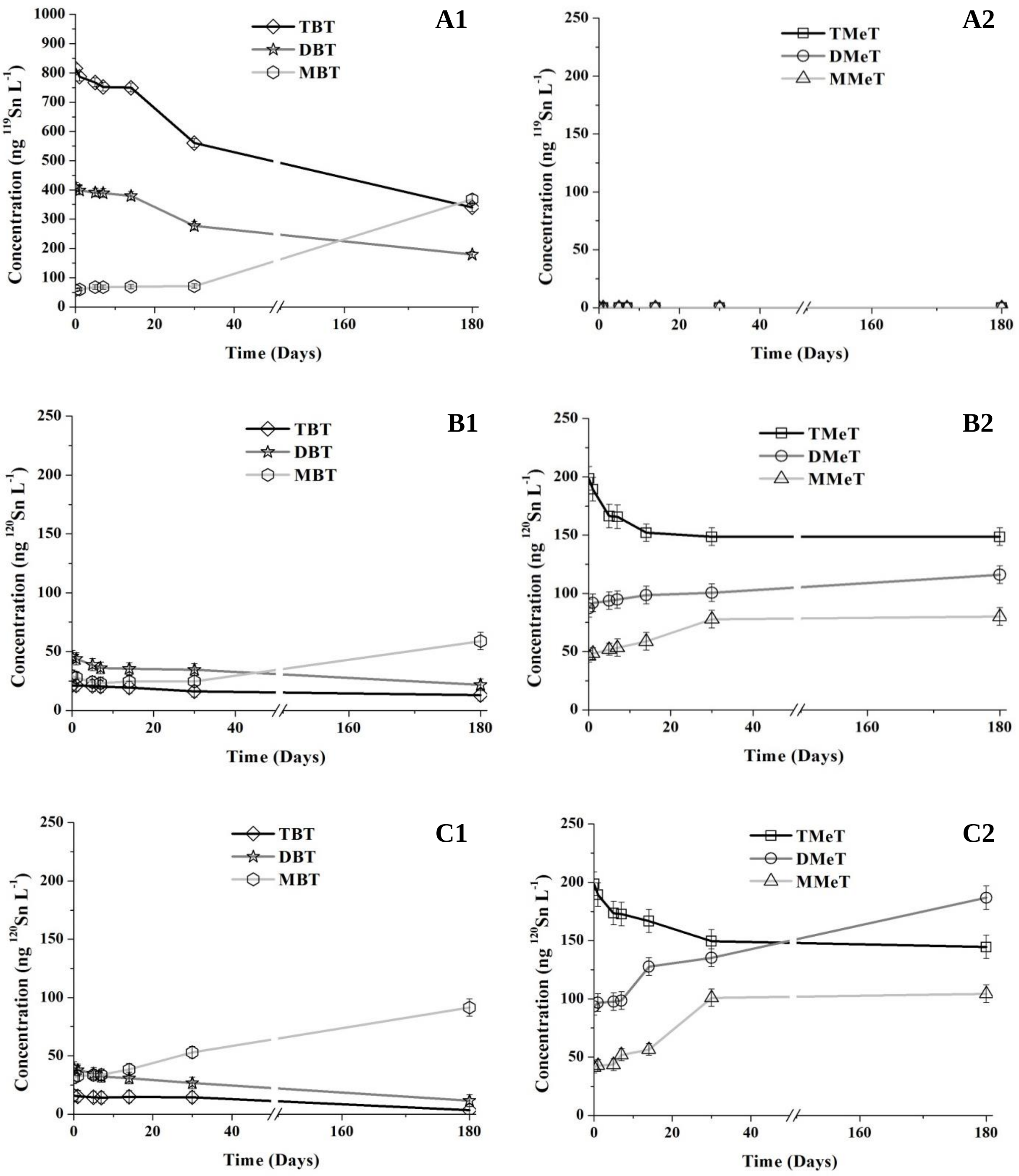

Figure 15: Transformation of OTCs in a landfill leachate over a time span of 6 months. The landfill leachate was spiked with ^{119}Sn-enriched butyltin mixture (815 ng Sn L^{-1} of TBT, 420 ng Sn L^{-1} of DBT and 60 ng Sn L^{-1} of MBT) and the concentrations were determined at *m/z* 119 for (A1) butyltin compounds and (A2) methyltin compounds, as well as at *m/z* 120 for (B1) butyltin compounds and (B2) methyltin compounds. The concentrations of the OTCs in an unspiked leachate were also determined at *m/z* 120 for (C1) butyltin compounds and (C2) methyltin compounds.

As can be seen from Figures 13A2, 14A2 and 15A2, methyltins were not formed from the added Sn-enriched butyltin spikes. Also no mixed methylbutyl species were detected. Vella and Adami (2001) observed the formation of mixed methylbutyl species in spiked marine sediment, but much higher concentrations of butyltins spikes were added (about 900 mg Sn L^{-1}), which are not likely to occur in environmental compartments.

From Figure 13A1 it may be seen that in house prepared ^{117}TBT contained also about 20 % of ^{117}DBT. Nevertheless, the transformation processes of ^{117}TBT can be followed. Extensive biodegradation of ^{117}TBT through a stepwise debutylation process is observed during the course of the experiment. Since, at the end of the experiment the sum of the concentrations of ^{117}Sn-enriched butyltins was lower than the starting concentration of the spike, it means that ^{117}MBT was, next to its formation, also progressively degraded to ionic tin.

In the leachate spiked with ^{119}DBT (Figure 14A1), a rapid degradation to ^{119}MBT occurred. The sum of ^{119}DBT and ^{119}MBT concentrations at the end of the experiment, which was lower than at the start, indicates the further degradation of ^{119}MBT to ionic tin. By comparing the degradation rate of ^{117}TBT and ^{119}DBT (Figures 13A1 and 14A1), it can be seen that the half-life of ^{117}TBT (22 days) was about twice that of ^{119}DBT (12 days). This indicates that the debutylation of ^{119}DBT occurred more rapidly than that of ^{117}TBT. These data are in accordance with the findings of Stasinakis et al. (2005) who studied the aerobic biodegradation of OTCs in activated sludge reactors. From Figures 13A1 and 14A1 it is further evident that the biodegradation rate of Sn-enriched MBT to inorganic tin is lower in the ^{119}DBT spiked leachate than the one with the ^{117}TBT spike. This phenomenon is most likely related to the catabolic degradation metabolism of butyl groups, which act as a source of carbon and energy for microorganisms (Stasinakis et al., 2005; Grady, 1984). Namely, the biodegradation process of ^{117}TBT releases a butyl group, which further serves as a source of energy to bacteria to degrade ^{117}DBT, releasing again a butyl group, which assists in the easier degradation of ^{117}MBT to inorganic tin. Since the available source of carbon for bacteria is higher in TBT than DBT, more effective stepwise degradation to inorganic tin was observed in ^{117}TBT spiked leachate.

In the leachate spiked with ^{119}Sn-enriched butyltin mix (Figure 15A1), a much slower degradation rate of ^{119}TBT and ^{119}DBT was observed than in the leachates spiked with ^{117}TBT or ^{119}DBT (Figures 13A1 and 14A1). The half-lives of ^{119}TBT and ^{119}DBT from the butyltin mix spike were reached approximately after six months. The inhibition of the biodegradation of OTCs was most probably associated to a higher toxicity of the butyltin mix to bacterial strains than the toxicity of TBT or DBT species, which were, as single spikes at approximately the same concentrations added to the leachates (Figures 13A1 and 14A1). The latter observations are in accordance with the reports of Dubey and Roy (2003) who stated that the biodegradation of OTCs by marine bacteria can be limited by the high toxicity of these compounds, to which only a few microorganisms are resistant.

The presumably lower toxicity of TBT or DBT to leachate biota, which were added as single Sn-enriched species in concentration of about 900 ng Sn L^{-1}, is evident not only from the much higher rates of degradation, but also from similar degradation pathways and methylation processes of the initially present OTCs in spiked and non-spiked leachates monitored at *m/z* 120 (Figures 13 and 14, rows B and C). On the contrary, in the landfill leachate spiked with ^{119}Sn-enriched butyltin mix, the degree of degradation of the initially present butyltins and methylation processes followed at *m/z* 120 (Figure 15, row B) is lower than that in the unspiked leachate (Figure 15, row C). The latter observation is most likely associated with the apparently higher toxicity of the butyltin mix spike towards the bacterial strains in the leachate. As a result, transformation processes are inhibited.

From the data of butyltins in unspiked leachates (graph C1 in Figures 13-15) it is evident that the initially present TBT and DBT degraded to MBT, which concentration was gradually increased during the course of the experiment. Since, at the start of the experiment, the concentrations of TBT and DBT were low, the available carbon energy source for bacteria was small. Due to that reason, a low degradation rate of MBT to inorganic tin was observed.

5.2.4 Role of living organisms in the transformation of organotin compounds in landfill leachates

In order to estimate the influence of the living organisms, present in the landfill leachate, on the transformation of OTCs, an additional experiment was performed as followed: one aliquot of leachate sample was sterilized in an autoclave (no living microorganisms), while the other was left non-sterilized (presence of microorganisms). Thereafter, 50 mL aliquots of sterilized and non-sterilized landfill leachates were transferred into amber glass containers. To follow the methylation processes from Sn^{2+} and Sn^{4+} species, the samples were spiked with ^{117}Sn-enriched Sn^{2+} and Sn^{4+} (100 ± 1 µg Sn L^{-1}) and left for 3 days. For the estimation of the degradation processes of butyltins, the samples were spiked with ^{117}TBT and ^{119}DBT species and left for 10 days. The composition of the ^{117}Sn-enriched TBT spike was 920 ± 40 ng Sn L^{-1} of TBT, 170 ± 10 ng Sn L^{-1} of DBT and 15 ± 1 ng Sn L^{-1} of MBT, while for the ^{119}Sn-enriched DBT spike the composition was 880 ± 40 ng Sn L^{-1} of DBT, 70 ± 5 ng Sn L^{-1} of MBT and < 0.9 ng Sn L^{-1} of TBT. To evaluate the influence of sterilization on OTC speciation, non-spiked sterilized and non-sterilized samples were also analysed. The results of these experiments are presented in Table 6 and Figure 16.

Table 6: Concentrations of ^{117}Sn-enriched MMeT in non-sterilized and sterilized leachate samples before spiking and 3 days after spiking with ^{117}Sn-enriched Sn^{2+} or Sn^{4+} (100 µg Sn L^{-1}). The concentrations of formed ^{117}Sn-enriched MMeT are also presented.

^{117}Sn-enriched spike	Sample treatment	^{117}Sn-enriched MMeT in leachate (ng Sn L^{-1})		
		Before spiking	3rd day after spiking	Formed
$^{117}Sn^{2+}$	Non-sterilized	10.2 ± 1.0	153 ± 15	143 ± 14
	Sterilized	8.3 ± 0.8	8.5 ± 0.8	0.17 ± 0.02
$^{117}Sn^{4+}$	Non-sterilized	10.2 ± 1.0	60 ± 6	49.8 ± 4.9
	Sterilized	8.3 ± 0.8	8.4 ± 0.8	0.10 ± 0.01

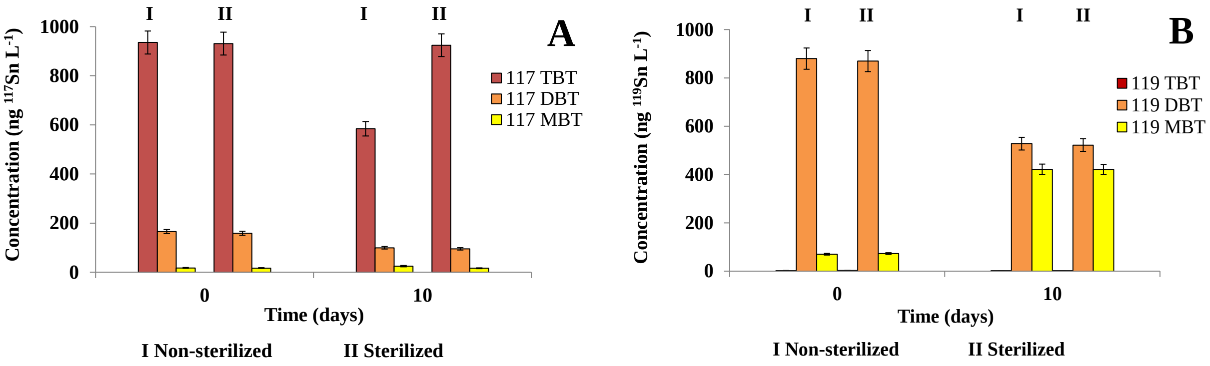

Figure 16: Transformation of butyltins in a landfill leachate over a time span of 10 days. The non-sterilized (I) and sterilized (II) landfill leachate samples were spiked with (A) ^{117}Sn-enriched TBT (920 ng Sn L^{-1} of TBT, 170 ng Sn L^{-1} of DBT, 15 ng Sn L^{-1} of MBT) and (B) ^{119}Sn-enriched DBT (880 ng Sn L^{-1} of DBT, 70 ng Sn L^{-1} of MBT, < 0.9 ng Sn L^{-1} of TBT). The concentrations were determined at *m/z* 117 (A) and *m/z* 119 (B).

The data of Table 6 demonstrate that 3 days after the addition of ^{117}Sn-enriched Sn^{2+} or Sn^{4+} species to non-sterilized samples of landfill leachate, only ^{117}MMeT species was formed in a concentration of 143 ng Sn L^{-1} from the ^{117}Sn-enriched Sn^{2+} spike and 49.8 ng Sn L^{-1} from the ^{117}Sn-enriched Sn^{4+} spike. The higher amount of ^{117}MMeT formed from Sn^{2+} in comparison to Sn^{4+} is related to the lower degree of hydrolysis of Sn^{2+}. By comparing the data of non-sterilized and sterilized samples before spiking, it can be seen, that after sterilization about 20 % of ^{117}MMeT was degraded. It is further evident that in sterilized samples ^{117}MMeT was not formed from the added ^{117}Sn-enriched Sn^{2+} or Sn^{4+} species. These data revealed that methylation in the landfill leachate is governed by microbial activity.

In the butyltins experiment (Figure 16) the influence of sterilization was negligible since their concentrations in the leachate were very low. From the data of Figure 16A, it can be seen that during the course of the experiment no degradation of ^{117}TBT is observed in sterilized spiked samples, while in non-sterilized samples about 40 % of ^{117}TBT added was degraded within 10 days. Based on these observations it may be concluded that the degradation of TBT in non-sterilized samples is governed by microorganisms. On the contrary, the data from Figure 16B show the same extent of degradation in non-sterilized and sterilized samples after spiking with ^{119}DBT, indicating the abiotic pathway of the degradation of DBT in landfill leachate samples.

5.3 ADSORPTION AND DEGRADATION PROCESSES OF TRIBUTYLTIN AND TRIMETHYLTIN IN LANDFILL LEACHATES TREATED WITH IRON NANOPARTICLES

Biotic and abiotic degradation of toxic OTCs in landfill leachates is usually not complete. To prevent environmental pollution, different remediation procedures such as flocculation or the use of various adsorbents have been applied. Nanotechnology offers new possibilities for remediation of contaminated sites (Joo and Cheng, 2006; Karn et al., 2009). Among different metal NPs, FeNPs exhibit a great potential for cost-effective remediation.

In the doctoral thesis, the potential of different FeNPs was evaluated for the removal of OTCs from landfill leachate. For this purpose, adsorption and degradation processes of TBT and TMeT in landfill leachates treated with nZVI, FeONPs and Fe_3O_4NPs, were investigated. It was hypothesized that at a basic pH, the studied OTCs will be removed by adsorption on the surface of FeNPs and the co-precipitation with iron corrosion products, while at an acidic pH, the degradation of OTCs by $OH^{\bullet}$, which are formed under aerated conditions in the presence of citric acid and dissolved Fe^{2+}, will occur.

To confirm these hypotheses, adsorption and degradation processes of TBT and TMeT were investigated in landfill leachate samples spiked with TBT and TMeT (1000 ng L^{-1} Sn). Their concentrations were similar to those observed at landfill sites around Europe (Mersiowsky et al., 2001; Pinel-Raffaitin et al., 2008). The spiked samples were treated, at pH 8 (the pH of the leachate) and pH 3 (adjusted with citric acid), with nZVI, FeONPs and Fe_3O_4NPs. Further inside to adsorption and degradation processes of TBT and TMeT was achieved by size fractionation of the samples. For this purpose sequential filtration of untreated leachates and landfill leachates treated with FeNPs was applied and the concentrations of OTCs were determined by GC-ICPMS.

For the investigation of the removal of OTCs by adsorption at pH 8, the leachate and the iron precipitate were analysed after the FeNPs treatment and the data compared with those of the untreated leachate.

To investigate the degradation of OTCs at pH 3, the leachate treated with citric acid and FeNPs, was analysed and the data were compared to those of the untreated leachate. At pH 3, FeNPs do not form iron corrosion products, while the adsorption on NPs is inhibited due to the presence of H^+ ions.

5.3.1 Adsorption and degradation of tributyltin and trimethyltin in spiked landfill leachates treated with nano zerovalent iron, iron oxide nanoparticles and magnetite nanoparticles

The potential of these different FeNPs was studied for the removal of TBT and TMeT from the landfill leachate at pH 8 and 3. The experiments were carried out under the conditions described in paragraph 4.4.3. TMAH was used for efficient dispersing of the FeNPs, and the treated leachate was shaken for 7 days. 7 days was chosen to ensure an efficient treatment.

The results obtained for the removal of TBT and TMeT with nZVI are presented in Figure 16 in the left and right column, respectively.

In untreated leachate at pH 8 (Figure 16A, left), about 20 % of the total TBT (the concentration in the leachate 2 days after spiking was 812 ng L^{-1} Sn) degraded into DBT and MBT. These data are in accordance with our previous findings on the biotic degradation of TBT in leachates (Peeters et al., 2014b). In addition, the TBT was not dissolved but was found mainly distributed among the fractions containing particles of 2.5 nm - 450 nm (about 55 %) and > 5000 nm (30 %).

After the nZVI treatment at pH 8 (Figure 16B, left), the total TBT concentration was reduced to 260 ng L^{-1} Sn. Furthermore, the amounts of TBT associated with leachate particles > 5 µm and in the fraction 2.5 nm - 450 nm, significantly decreased compared to the untreated leachate, for about 20 and 2 times, respectively. This decrease was not associated to an increase of DBT and MBT concentrations; the total concentration of DBT being even decreased for about 65 % compared to the untreated leachate. The analysis of OTCs in the precipitate confirmed the presence of TBT, DBT and MBT. The sum of the concentrations of OTCs, which remained in the solution and OTCs adsorbed onto the iron precipitate after the nZVI treatment, was the same as the concentration of the untreated leachate after 7 days. All OTCs were precipitated with iron corrosion products.

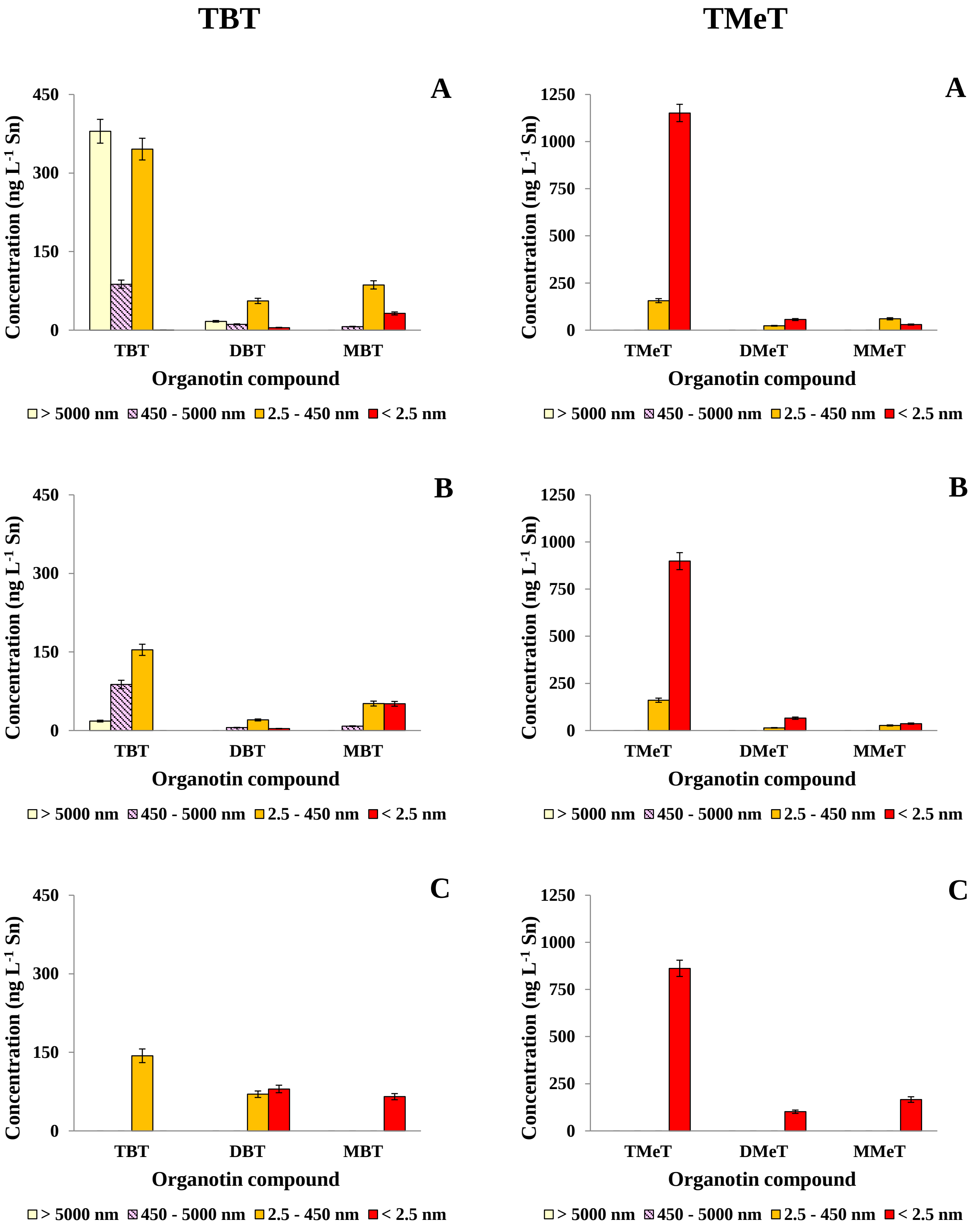

Figure 17: Size distribution of OTCs in landfill leachates. (A) The untreated leachates (pH 8) were spiked with TBT (1000 ng Sn L^{-1}) or TMeT (1000 ng Sn L^{-1}). (B) The spiked leachates (pH 8) were treated with nZVI. (C) The pH of the spiked leachates was adjusted to 3 with citric acid and the samples were treated with nZVI. nZVI was dispersed with TMAH.

When the nZVI treatment was performed at pH 3 (Figure 17C, left), about 17 % of the total TBT, which was initially present in the untreated leachate, was found and only in the fraction 2.5 nm - 450 nm. In addition, the total concentration of DBT increased slightly in comparison to the untreated leachate, while the total concentration of MBT was slightly decreased. The present observations indicate that TBT was mainly degraded by successive debutylations, which is most likely a consequence of the formation of $OH^{\bullet}$ radicals via a Fenton-type reaction in the presence of nZVI and citric acid. In comparison to the adsorption process by nZVI treatment at pH 8, the degradation of TBT more effectively removes this contaminant from the leachate.

In the untreated leachate at pH 8, the total concentration of methyltins after spiking with TMeT (1000 ng L^{-1} Sn) was 1475 ng L^{-1} Sn, since TMeT (about 300 ng L^{-1} Sn) and smaller amounts of dimethyltin (DMeT) and monomethyltin (MMeT) (less than 100 ng L^{-1} Sn, each) were originally present in the analysed leachate. After spiking, 90 % of TMeT was present in the leachate fraction with particles smaller than 2.5 nm and 10 % in the fraction 2.5 nm - 450 nm (Figure 17A, right). After the nZVI treatment at pH 8 (Figure 17B, right), the total TMeT concentration was reduced for about 20 %, due to the adsorption of TMeT onto the surface of nZVI, which was confirmed by the analysis of methyltins in the precipitate. When the spiked leachate was treated with nZVI at pH 3 (Figure 17C, right), the originally present TMeT in the fraction with particles 2.5 nm - 450 nm, disappeared by degradation. The remaining TMeT in the fraction with particles < 2.5 nm represented about 75 % of its total content in the spiked leachate. Hence, the degradation of TMeT at pH 3 was less effective than that of TBT. Our experimental data revealed that TMeT was a hardly degradable species, as are some other organic compounds (Deng and Englehardt, 2006).

The same experiments as with nZVI were performed to examine the potential of TBT and TMeT removal from landfill leachate by the use of FeONPs and Fe_3O_4NPs at pH 8 and 3. TMAH was used for the dispersion of FeNPs. The results presented in Figures 18 and 19 demonstrate a similar extent of TBT removal at pH 8 and 3 with both FeONPs and Fe_3O_4NPs, as when the leachate was treated with nZVI. Also, the level of TMeT removal governed by adsorption (pH 8) and degradation (pH 3) is similar for all three investigated FeNPs. So, in the following experiments only nZVI was used.

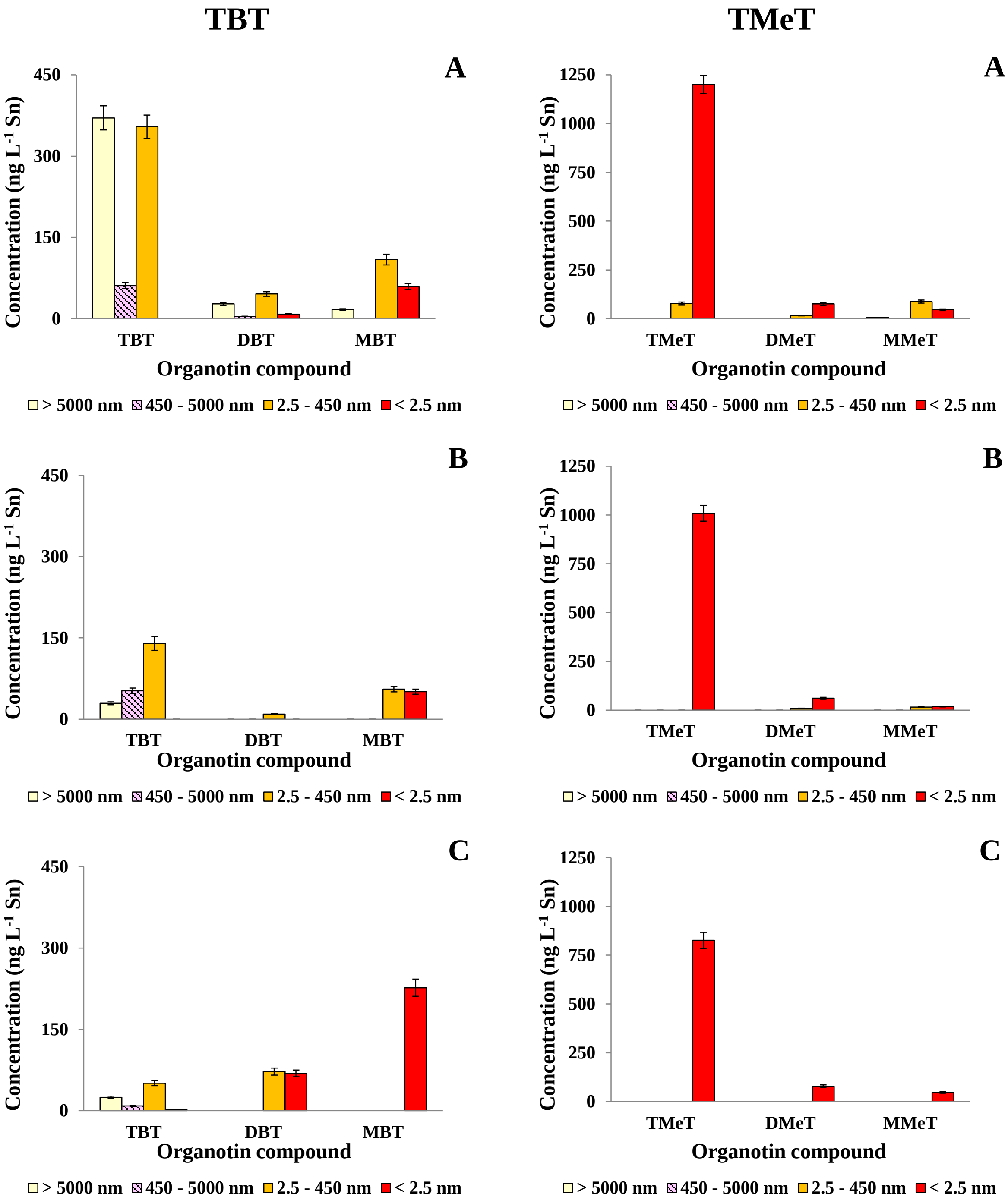

Figure 18: Size distribution of OTCs in landfill leachates. (A) The untreated leachates (pH 8) were spiked with TBT (1000 ng Sn L^{-1}) or TMeT (1000 ng Sn L^{-1}). (B) The spiked leachates (pH 8) were treated with FeONPs. (C) The pH of the spiked leachates was adjusted to 3 with citric acid and the samples were treated with FeONPs. FeONPs were dispersed with TMAH.

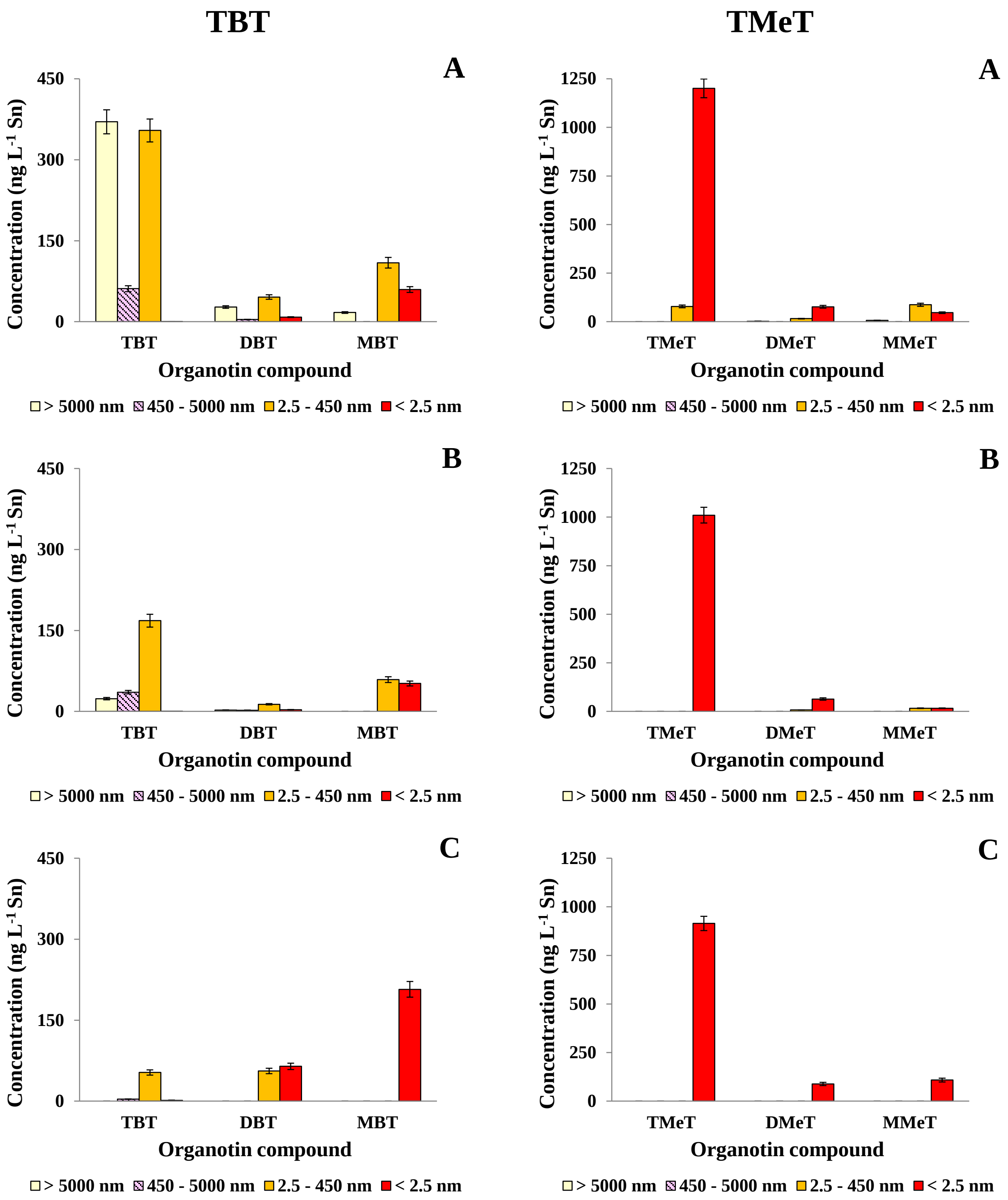

Figure 19: Size distribution of OTCs in landfill leachates. (A) The untreated leachates (pH 8) were spiked with TBT (1000 ng Sn L^{-1}) or TMeT (1000 ng Sn L^{-1}). (B) The spiked leachates (pH 8) were treated with Fe_3O_4NPs. (C) The pH of the spiked leachates was adjusted to 3 with citric acid and the samples were treated with Fe_3O_4NPs. Fe_3O_4NPs were dispersed with TMAH.

5.3.2 Sequential removal of tributyltin and trimethyltin in landfill leachate treated with nano zerovalent iron

In order to further improve the removal of TBT and TMeT, a two-step sequential leachate treatment with nZVI was investigated, combining adsorption and degradation processes. nZVI was dispersed with TMAH. The sequential procedure was planned so, that the treatment time did not exceed a duration of 7 days. The leachate samples, spiked with TBT or TMeT, were first treated with nZVI at pH 8 and shaken for 3 days. The iron precipitate was separated from the leachate by a magnet. Then, in one sample aliquot sequential filtration was applied, while in another, the pH was adjusted to pH 3 with citric acid. The sample was again treated with nZVI, shaken for 3 days extra and sequential filtration was performed prior to the determination of OTCs in the different fractions. Such a procedure allows the estimation of the removal efficiency of OTCs in each step.

The results of these experiments are presented in Figure 20, where graphs A for TBT (left) and TMeT (right) represent the untreated leachate at pH 8.

The efficiency of TBT removal at pH 8 is similar when the leachate is treated with nZVI for 3 days (Figure 20B, left) or for 7 days (Figure 17B, left), meaning that also the shorter treatment time of 3 days is adequate. The data of Figure 20C (left) indicate that a sequential treatment of the leachate, combining adsorption-precipitation (pH 8) and degradation (pH 3), more effectively removed TBT (the extent of TBT removal was about 91 %) than when the leachate was only treated by nZVI at pH 3 (the extent of TBT degradation was about 83 %, Figure 17C, left). For TMeT (Figure 20B and 20C, right), it is evident that a sequential treatment with nZVI has almost no influence on the efficiency of its removal from the leachate.

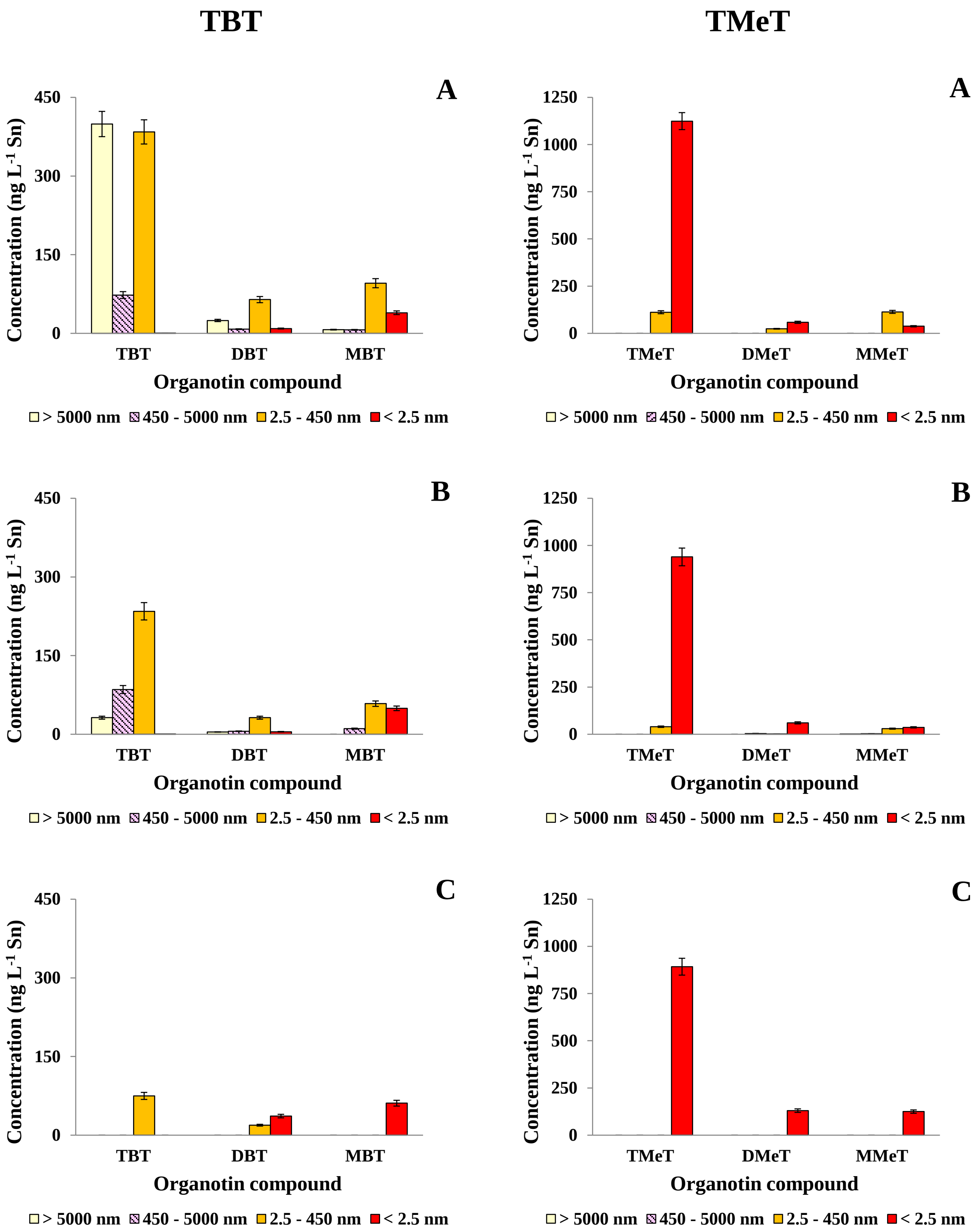

Figure 20: Size distribution of OTCs in landfill leachates. (A) The untreated leachates (pH 8) were spiked with TBT (1000 ng Sn L^{-1}) or TMeT (1000 ng Sn L^{-1}). (B) The spiked leachates (pH 8) were treated with nZVI. (C) The spiked leachates (pH 8) were first treated with nZVI, the iron precipitate was removed, the pH was adjusted to 3 with citric acid and the samples were again treated with nZVI. nZVI was dispersed with TMAH.

5.3.3 Investigation of the degradation processes

In order to confirm that the degradation of the analysed OTCs at pH 3 is not a biotic but primarily an abiotic process, governed by Fenton chemistry, additional experiments were carried out. The leachate samples spiked with TBT or TMeT were first treated with nZVI (dispersed with TMAH) at pH 8. After the removal of iron, one sample aliquot was sterilized, while the other was kept non-sterilized. To the sterilized and non-sterilized samples, citric acid was added or a combined treatment (a combination of citric acid and nZVI) was applied. The results are presented in Figure 21, where graph A represents the untreated leachate spiked with TBT at pH 8, and graph B, the leachate spiked with TBT and treated with nZVI at pH 8.

When only citric acid was added (Figures 21C1 and 21C2), substantial degradation of TBT was observed. It should be pointed out that the amount of iron in the dissolved and nanosized fractions, which remained after the removal of nZVI precipitate in the leachate (about 1.5 mg L^{-1} Fe), was high enough to provoke the degradation of TBT in the presence of citric acid and dissolved oxygen. It was also experimentally proven that citric acid alone is not able to degrade TBT in an aqueous solution, which does not contain iron (these data are not shown). In the sterilized leachate samples (Figure 21C1) almost 99 % of TBT was removed, and in the non-sterilized samples (Figure 21C2) about 88 %. The less effective degradation of TBT in non-sterilized samples is probably related to the microbial degradation of citric acid (SIDS Initial assessment report for 11th SIAM, 2001), thus decreasing its content available for Fenton chemistry. The same extent of TBT removal (98 %) as in sterilized leachate samples with the addition of citric acid (Figure 21C1), was observed in sterilized leachate, where citric acid and nZVI were both added (Figure 21D1). The removal of TBT in non-sterilized samples, after the sequential treatment with nZVI at pH 8 and pH 3, was slightly more effective (about 92 %) (Figure 21D2) than in the samples to which, after the treatment with nZVI at pH 8 (Figure 21C2), only citric acid was added. In the sterilized samples not only TBT, but also DBT and MBT were more effectively degraded than in the non-sterilized samples.

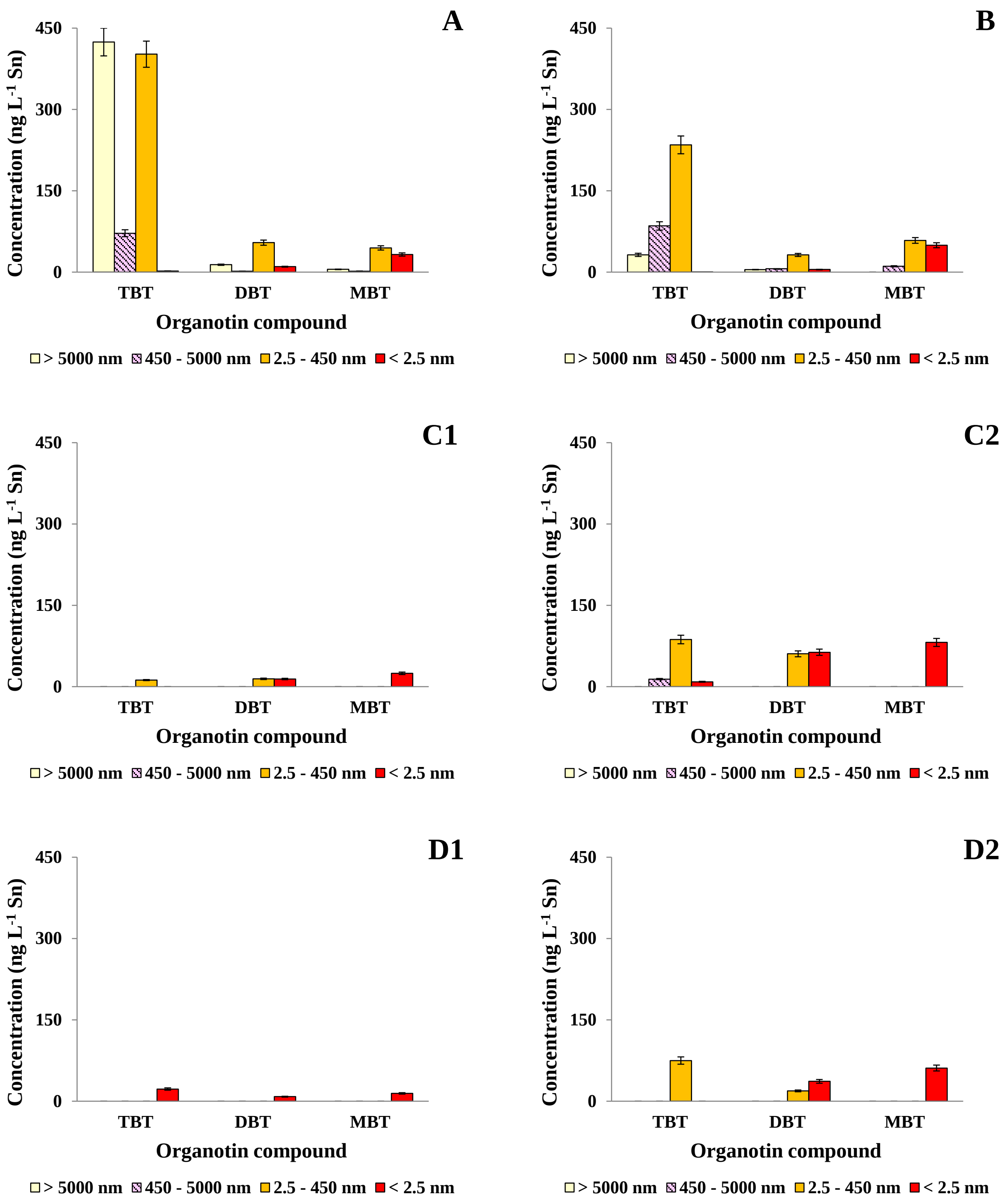

Figure 21: Size distribution of butyltins in landfill leachates. (A) The untreated leachates (pH 8) were spiked with TBT (1000 ng Sn L^{-1}). (B) The spiked leachates (pH 8) were treated with nZVI. (C) The spiked leachates (pH 8) were first treated with nZVI, the iron precipitate was removed and the pH of the sterilized samples (1) and non-sterilized samples (2) was adjusted to 3 with citric acid. (D) The spiked leachates (pH 8) were first treated with nZVI, the iron precipitate was removed and the pH of the sterilized samples (1) and non-sterilized samples (2) was adjusted to 3 with citric acid and the samples were again treated with nZVI. nZVI was dispersed with TMAH.

The data presented in Figure 22 exhibit the same extent of removal of TMeT in the sterilized and non-sterilized samples (about 35 %) for both, when the leachate was, after the nZVI treatment at pH 8, treated with only citric acid or with citric acid and nZVI.

The experiments described above confirmed that, under aerated conditions in the leachate treated with nZVI in the presence of citric acid (pH 3), the degradation of TBT and TMeT is governed primarily by the Fenton process.

To check whether citric acid alone (without addition of nZVI) provokes the degradation of OTCs in leachate, samples were spiked with TBT or TMeT, citric acid was added and the samples were shaken under aerated conditions for 3 days. The concentration of dissolved and nanosized iron, originally present in the leachate, was about 1.5 mg L^{-1} Fe. The results presented in Figure 23 indicate that about 75 % of TBT was degraded after the addition of citric acid. A significant increase in the DBT concentration, in an amount equal to the content of the degraded TBT, was observed. By comparing these data with the obtained results, when the leachate was sequentially treated with nZVI (pH 8) followed by treatment with citric acid and nZVI (pH 3) (Figure 21D2), the nZVI treatment is, regarding the TBT degradation much more effective, because it also effectively degrades DBT. The results presented in Figure 23, further demonstrated that the addition of citric acid to the leachate has no influence on the degradation of TMeT.

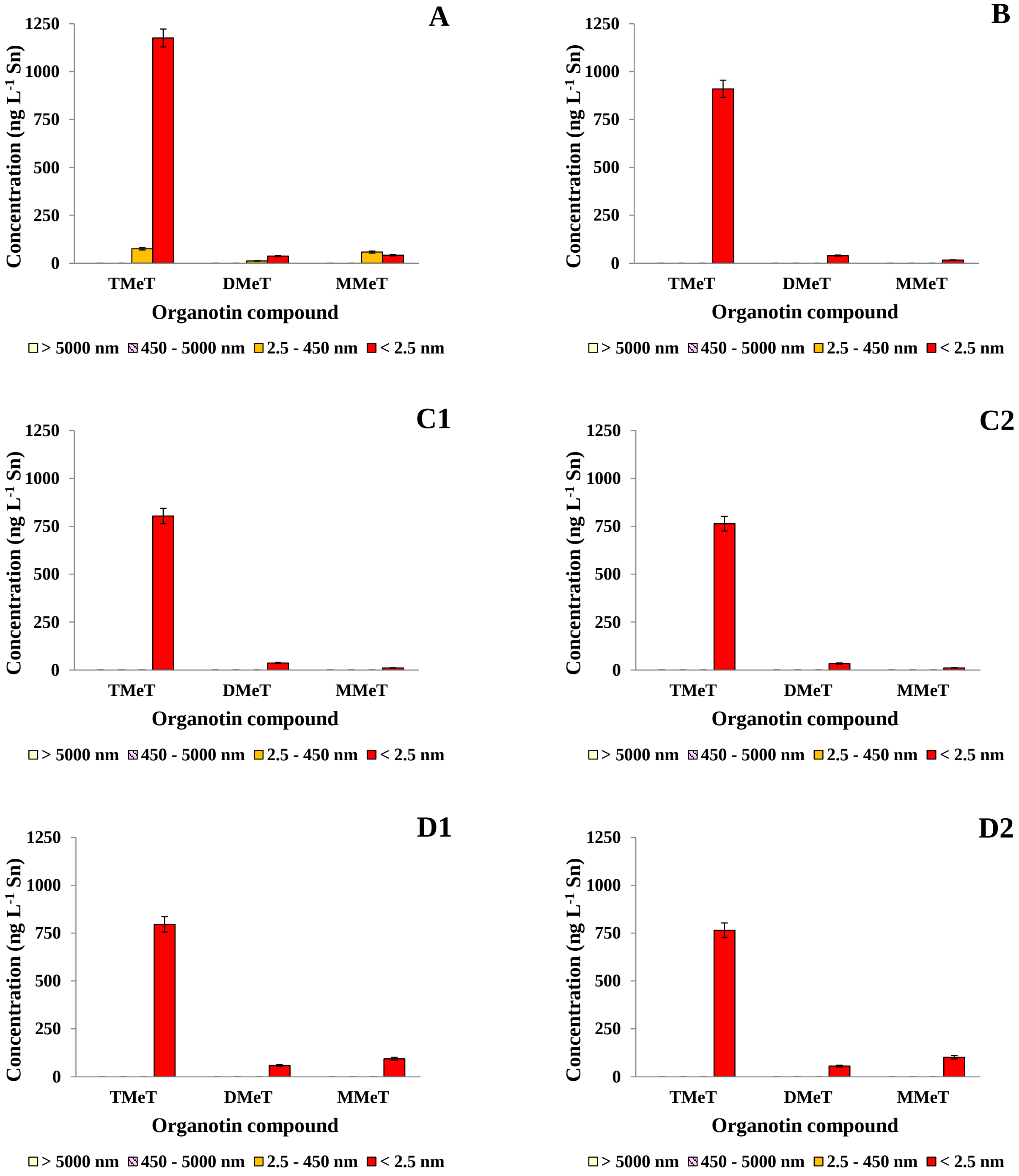

Figure 22: Size distribution of methyltins in landfill leachates. (A) The untreated leachates (pH 8) were spiked with TMeT (1000 ng Sn L^{-1}). (B) The spiked leachates (pH 8) were treated with nZVI. (C) The spiked leachates (pH 8) were first treated with nZVI, the iron precipitate was removed and the pH of the sterilized samples (1) and non-sterilized samples (2) was adjusted to 3 with citric acid. (D) The spiked leachates (pH 8) were first treated with nZVI, the iron precipitate was removed and the pH of the sterilized samples (1) and non-sterilized samples (2) was adjusted to 3 with citric acid and the samples were again treated with nZVI. nZVI was dispersed with TMAH.

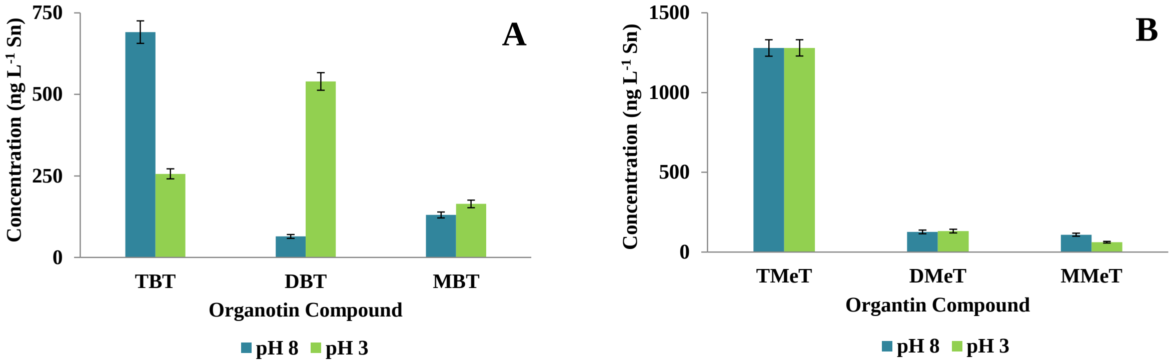

Figure 23: Speciation of OTCs in landfill leachates, at pH 8 or pH 3, spiked with (A) TBT (1000 ng Sn L^{-1}) or (B) TMeT (1000 ng Sn L^{-1}). After spiking, the samples were shaken for 2 days before being analysed. The pH was adjusted to 3 with citric acid.

5.3.4 Influence of tetramethylammonium hydroxide used for dispersion of iron nanoparticles on methylation processes in the leachate

In the experiments where leachate samples were spiked with TMeT and the pH was adjusted to 3 with citric acid, followed by a treatment with FeNPs using TMAH for dispersion, formation of MMeT was observed (see data of Figs. 17C, 20C, 22D). The same phenomenon of the transformation of methyltin species, which were originally present in the leachate, was also observed in the samples spiked with TBT at pH 3, after the treatment of the leachate with nZVI (Fig. 24C). The concentration of the formed MMeT in the leachate, which was treated with nZVI, was about 110 ng L^{-1} Sn (Compare the data of Figures 24C and 24A). To find out whether MMeT appeared as a consequence of the degradation of TMeT or is a newly formed species by the abiotic methylation of inorganic tin (the tin concentration in the leachate was about 80 µg L^{-1}), new sets of experiments were performed. Leachate samples were spiked with TBT or TMeT and a sequential treatment of the leachate with nZVI was carried out at pH 8 and 3. nZVI were dispersed by mixing, or TMAH was used as dispersing agent. In these experiments, the efficiency of the degradation of TBT and TMeT by the use of different modes of dispersion was also tested. The results are presented in Figure 25.

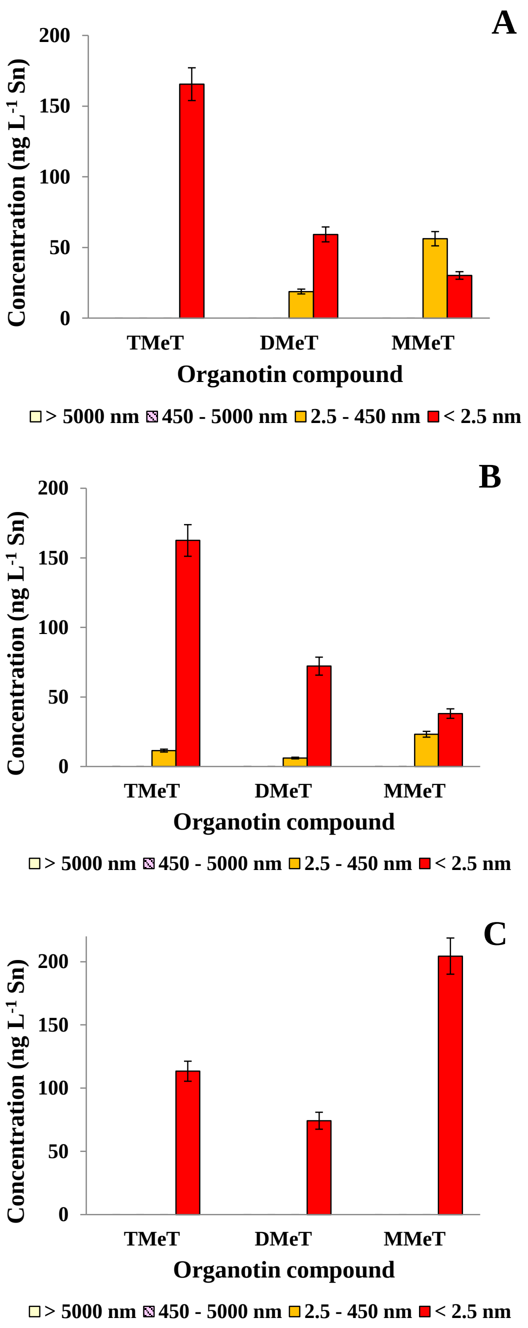

Figure 24: Size distribution of methyltins in landfill leachates, spiked with TBT (1000 ng Sn L^{-1}) and treated with nZVI. (A) Untreated spiked leachates (pH 8). (B) The spiked leachates (pH 8) were treated with nZVI. (C) The pH of the spiked leachates was adjusted to 3 with citric acid and the sample was treated with nZVI. nZVI was dispersed with TMAH.

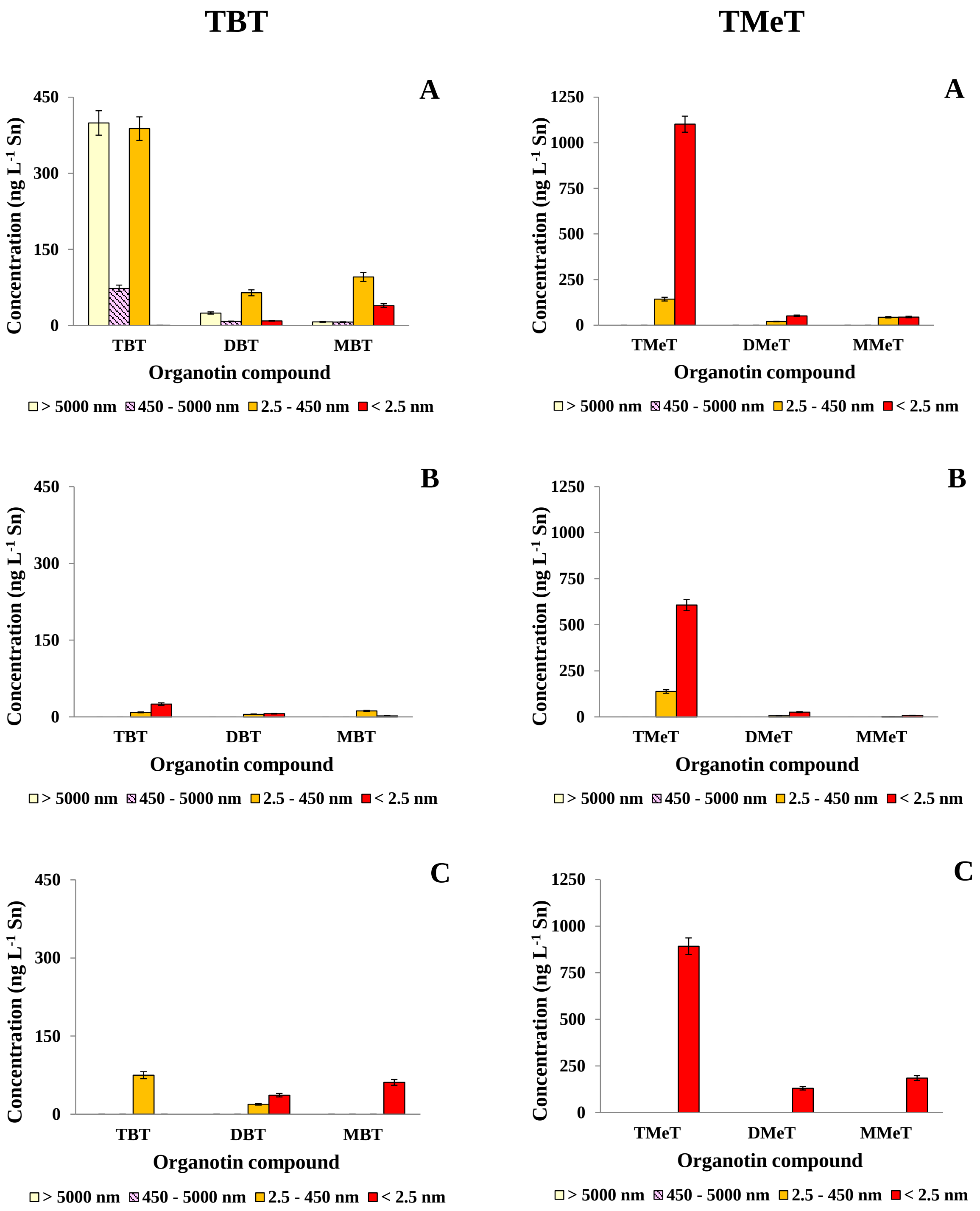

Figure 25: Size distribution of OTCs in landfill leachates. (A) The untreated leachates (pH 8) were spiked with TBT (1000 ng Sn L^{-1}) or TMeT (1000 ng Sn L^{-1}). (B) The spiked leachates (pH 8) were first treated with nZVI, the iron precipitate was removed, the pH of the sample was adjusted to 3 with citric acid and the samples were again treated with nZVI. nZVI was dispersed by mixing.(C) The spiked leachates (pH 8) were first treated with nZVI, the iron precipitate was removed, the pH of the sample was adjusted to 3 with citric acid and the samples were again treated with nZVI. nZVI was dispersed with TMAH.

From the data of Figure 25, it is evident that the degradation of TBT and TMeT is more effective when nZVI is dispersed by mixing. As a result of a higher reactivity of the NPs, 96 % of TBT and more than 90 % of DBT and MBT was removed by the sequential treatment of the leachate with nZVI when mixing was applied for dispersion (Figure 25B, left). When TMAH was used as a dispersing agent about 90 %, 50 % and 60 % of TBT, DBT and MBT, respectively were removed (Figure 25C, left). Regarding the removal of methyltins, about 40 % of TMeT, 45 % of DMeT and 90 % of MMeT was removed when mixing was used for dispersion (Figure 25B, right). Although TMAH disperses more efficiently nZVI, it modifies also the surface of the NPs so that they became less reactive. The decrease in the reactivity of nZVI was observed also in previous studies with silica coated and choline modified nZVI (Kržišnik et al., 2014).

When nZVI was dispersed by TMAH, about 30 % of TMeT was removed from the leachate, while DMeT and MMeT were not removed, but formed in concentrations of about 60 and 100 ng L^{-1} Sn, respectively (Figure 25C, right). By comparing the data of Figures 25B and 25C (right), it is clearly evident that TMAH in the presence of citric acid provokes abiotic methylation. Such an abiotic methylation was also observed by other investigators, for the methylation of mercury during its extraction procedure (Qvarnström and Frech, 2002). To avoid the abiotic formation of highly toxic methylmercury and methyltin species in the leachate, the use of TMAH for dispersion of nZVI, in the presence of citric acid, should be omitted.

5.4 FATE OF IRON NANOPARTICLES IN ENVIRONMENTAL WATERS TREATED WITH NANOSCALE ZEROVALENT IRON, IRON OXIDE NANOPARTICLES AND MAGNETITE NANOPARTICLES

FeNPs are increasingly used to remove different pollutants from contaminated environmental waters (Krajangpan et al., 2009; Noubactep, 2010; Singh et al., 2012; Palanisamy et al., 2013). At neutral to alkaline pHs, adsorption of pollutants onto the surface of FeNPs and co-precipitation with iron corrosion products is the prevailing process of pollutant removal (Noubactep, 2010). During the remediation, iron corrosion products are formed and precipitated. In this way, FeNPs lose their nano-character. To prevent the potential toxic effects of the remaining FeNPs towards biota in environmental waters, it is necessary to follow their fate after the treatment. Ionic strength, the content of organic matter and the use of dispersing agents significantly influence the behaviour of NPs (Jiang et al., 2009; Bian et al., 2011; Hu et al., 2010; Hotze et al., 2010). Although it is important to understand the behaviour of NPs after the remediation, the literature data addressing this issue are scarce. The reports are mainly related to toxicological studies (Auffan et al., 2008; Grieger et al., 2008; Karthikeyeni et al., 2013). So, in the doctoral thesis, the investigation was oriented to study the size distribution of different FeNPs after the treatment of environmental water samples.

5.4.1 Size distribution of particles in environmental waters treated with different iron nanoparticles

The fate of FeNPs in Milli Q water, forest spring water and landfill leachate treated with nZVI, FeONPs and Fe_3O_4NPs was investigated over a time span from 15 min to 24 h after the treatment with FeNPs. FeNPs were dispersed with TMAH or by mixing. The sample preparation is described in details under paragraph 4.3.4.

5.4.1.1 Milli Q water

First, the behaviour of NPs in Milli Q water treated with FeNPs was investigated. As can be seen from the data of Table 7, Milli Q water has an extremely low electrical conductivity (which is related to a low ionic strength) and contains negligible content of organic matter. In such an aqueous matrix, the interactions that are caused by the presence of organic matter or ionic strength are totally negligible.

To follow the size distribution of FeNPs, sequential filtration of samples was applied. The results for the time dependent size distribution of iron in Milli Q water treated with nZVI, FeONPs and Fe_3O_4NPs, are presented in Figure 26.

Table 7: Sample characteristics of aqueous samples.

Sample	Electrical conductivity (µS cm^{-1})	Total organic content (mg L^{-1})	Dissolved organic content (mg L^{-1})	pH
Milli Q water	0.055 ± 0.001	< 0.005	< 0.005	5.5 ± 0.1
Forest spring water	58 ± 1	45 ± 1	38 ± 1	5.5± 0.1
Landfill leachate	6800 ± 100	760 ± 15	690 ± 15	8.0 ± 0.1

The data from Figure 26 demonstrate that the dispersion of FeNPs with TMAH (left column) is much more effective than by mixing (right column). TMAH acts as a surfactant and creates an electrostatic repulsion layer around nZVI and Fe_3O_4NPS, keeping them dispersed in solution (Andrade et al., 2012; Tang and Lo, 2013). FeONPs coated with a layer of oleic acid possess hydrophobic characteristics and are dispersed in heptane by steric interactions (Scherer and Figueiredo Neto, 2005). TMAH is frequently used as a surfactant that changes the surface properties of NPs. It forms a strong electrostatic ligand bilayer that allows the transfer of the otherwise hydrophobic NPs to water. The double layer around NPs also inhibits the oxidation of FeONPs (Sperling and Park, 2010).

When Milli Q water was treated with nZVI, using TMAH for dispersion (Figure 26A1), it is expected that iron corrosion products, generated by a rapid reaction of Fe^{2+} (formed from Fe^0) with dissolved oxygen, aggregated and precipitated in a short time. As a confirmation, an iron precipitate in Milli Q water treated with nZVI, was immediately observed after shaking was stopped. The coarser iron particles (450 – 5000 nm) were mainly settled within 4 h, while those with sizes 2.5 – 100 nm and 100 – 200 nm persisted even 24 h after the nZVI treatment in the solution. However, the iron concentrations in these both fractions were low and did not exceed 1 mg L^{-1} Fe.

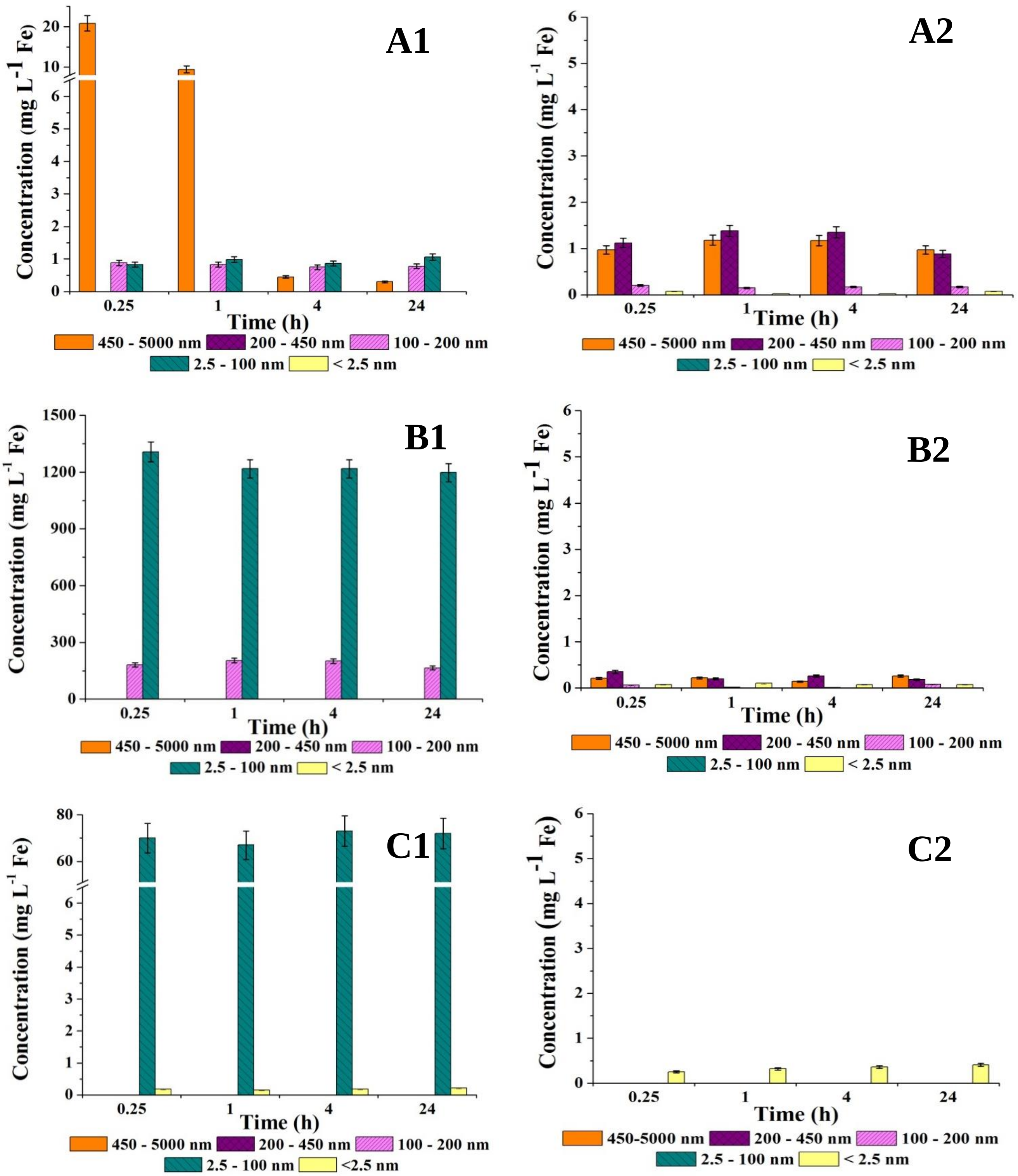

Figure 26: Time dependent size distribution of iron in Milli Q water treated with nZVI (A), FeONPs (B) and Fe_3O_4NPs (C). The FeNPs (iron load 1.5 g L^{-1}) were dispersed with TMAH (1) or by mixing (2). The concentration of iron in the fractions obtained by the sequential filtration of the samples was determined by ICPMS. The error bars represent the experimental and analytical uncertainty.

In Milli Q water treated with FeONPs, using TMAH for dispersion (Figure 26B1), iron precipitate was not observed. FeONPs remained dispersed in solution for longer than 24 h after the treatment. The prevailing iron containing fraction was that with particles of 2.5 - 100 nm (about 1300 mg L^{-1} Fe), followed by the fraction with particles of 100 - 200 nm (about 200 mg L^{-1} Fe). The reason is that, FeONPs coated with oleic acid, were after the addition of TMAH, efficiently dispersed in Milli Q water by strong electrosteric interactions (Sperling and Park, 2010; Tang and Lo, 2013). Their oxidation and consequently the formation of iron corrosion products were inhibited by a bilayer of oleic acid and TMAH, which covered NPs.

When Milli Q water was treated with Fe_3O_4NPs (Figure 26C1), iron precipitate was observed immediately after shaking was stopped. Since the reactivity of Fe_3O_4NPs is much lower than that of nZVI, iron corrosion products were not so effectively formed. Consequently, 24 h after the Fe_3O_4NPs treatment, about 75 mg L^{-1} Fe remained in the nanosized fraction 2.5 - 100 nm, while very low iron concentration (about 0.2 mg L^{-1} Fe) was also determined in the dissolved fraction (particle sizes < 2.5 nm).

The dispersion of FeNPS by mixing was not as efficient as by TMAH. When mixing was applied to disperse nZVI or Fe_3O_4NPs in Milli Q water, an iron precipitate was observed as soon as the shaking was stopped. For Fe_3O_4NPs only a negligible fraction of iron (about 0.2 mg L^{-1} Fe) remained dissolved in solution (Figure 26C2), while a slightly higher amount of nZVI (about 1.0 mg L^{-1} Fe) remained dispersed during the course of the experiment (Figure 26A2).

Oleic acid coated FeONPs are hydrophobic, instead of being dispersed, FeONPs were stuck on the surface of the glass containers. As evident from Figure 26B2 only a negligible portion of nanosized iron remained in solution during the course of the experiment (about 0.3 mg L^{-1} Fe).

5.4.1.2 Forest spring water

Forest spring water is a sample matrix with both, a low ionic strength (which is reflected by a low electrical conductivity) and a low content of dissolved and total organic matter (see data of Table 7). The iron concentration in the samples of forest spring water was below 0.3 mg L^{-1} Fe, distributed in fractions between 2.5 – 100 nm and < 2.5 nm. The behaviour of NPs in this water in which FeNPs were added using TMAH or mixing for dispersion, is presented in Figure 27.

When TMAH was used for the dispersion of nZVI or Fe_3O_4NPs in forest spring water, the positively charged quaternary ammonium ions reacted with the deprotonated carboxylic groups of organic acids (constituents of organic matter), forming quaternary ammonium salts of the carboxylate anions (Kossa et al., 1979). As a consequence of these reactions, the TMAH dispersion property was lost. nZVI and Fe_3O_4NPs were not efficiently dispersed but agglomerated and precipitated as soon as shaking was stopped (Figures 27A1and 27C1).

On the contratry, for FeONPs dispersed by TMAH (Figure 27B1), iron precipitate was not observed since a bilayer of oleic acid and TMAH inhibited the oxidation of FeO and formation of iron corrosion products. NPs remained dispersed in solution for at least 24 h after the FeONPs treatment, exclusively in the fraction with particle sizes 2.5 – 100 nm. This phenomenon can be explained by a strong interaction that occurred between oleic acid and TMAH, which prevented desorption of TMAH from the surface of FeONPs and therby its reaction with dissolved organic matter. TMAH remained to act as a dispersing agent, while the surfactans, which were originally present in the samples, additionally enhanced the dispersion efficiency (Maurer-Jones et al., 2013).

When mixing was used for the dispersion of FeNPs, the surfactants has no observable effect on the efficiency of dispersion of nZVI or Fe_3O_4NPs (Figures 27A2 and 27C2). A slight enhancement in the dispersion efficiency was observed for FeONPs. In this case, the originally present surfactants interacted with oleic acid and, as a result, small amounts of iron in particles bigger that 100 nm, remained dispersed in samples for at least 24 h after shaking was stopped.

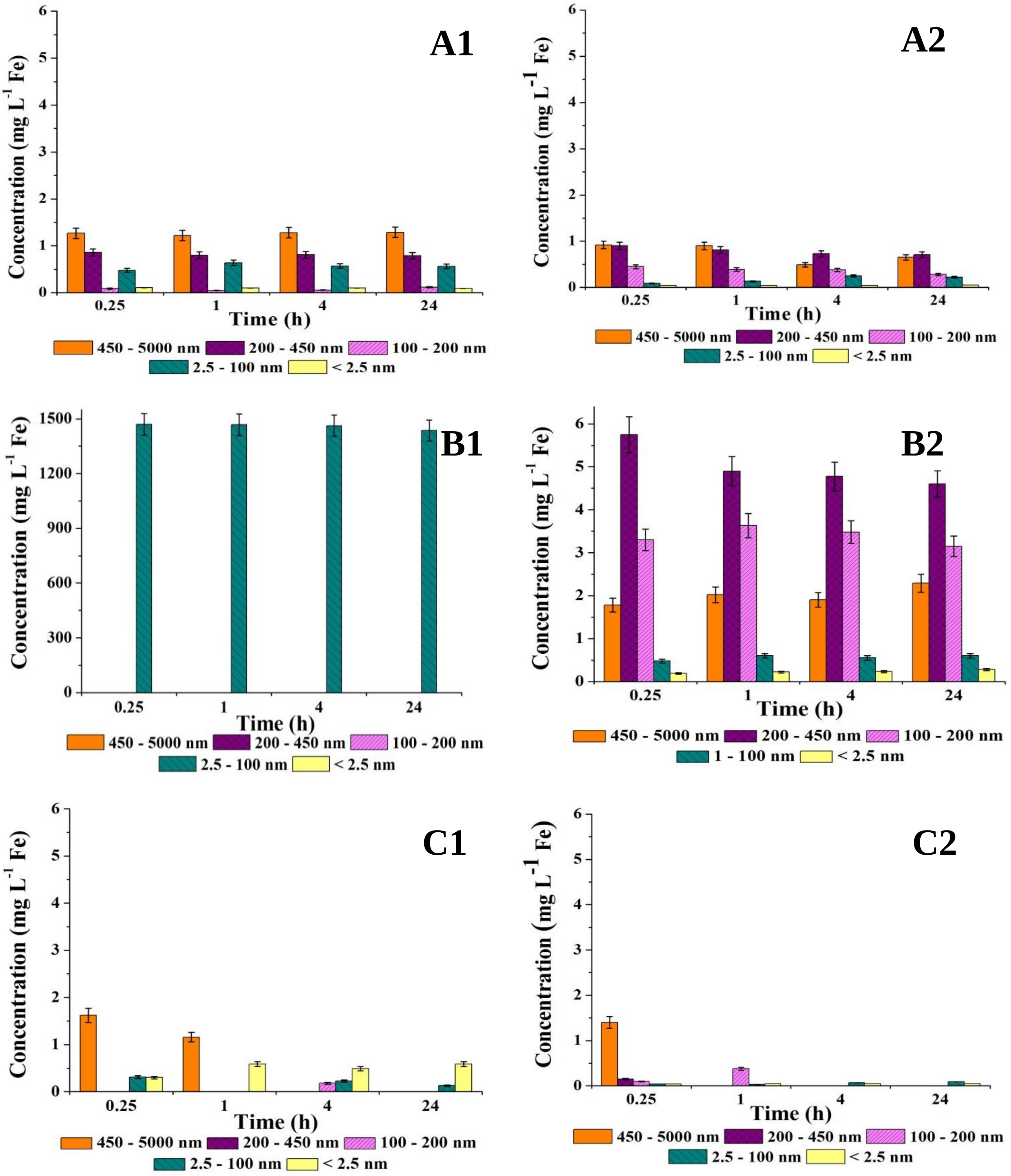

Figure 27: Time dependent size distribution of iron in forest spring water treated with nZVI (A), FeONPs (B) and Fe_3O_4NPs (C). The FeNPs (iron load 1.5 g L^{-1}) were dispersed with TMAH (1) or by mixing (2). The concentration of iron in the fractions obtained by the sequential filtration of the samples was determined by ICPMS. The error bars represent the experimental and analytical uncertainty.

5.4.1.3 Landfill leachate

A landfill leachate represents a sample matrix with a very high ionic strength (which is reflected by a high electrical conductivity) and a high content of dissolved and total organic matter (see data of Table 7). The iron concentration was about 2 mg L^{-1} Fe. It was distributed between fractions 2.5 – 100 nm (0.5 mg L^{-1} Fe) and < 2.5 nm (1.5 mg L^{-1} Fe). The behaviour of NPs in landfill leachate treated with FeNPs, using TMAH or mixing for dispersion, is presented in Figure 28.

Once added to the landfill leachate, the behaviour of FeNPs depends on the combination of several processes. As explained previously, there is a significant increased tendency to agglomerate and to settle down. Contrary to this, the excess of surfactants and dissolved organic matter, which did not react with TMAH, forms a coating around FeNPs, which acts as a surfactant that keeps them dispersed in solution. Another influence comes from the high ionic strength of the sample matrix. It causes the aggregation of FeNPs by reducing the repulsive forces between NPs and the size of the electrostatic layer around them (Hotze et al., 2010). The results presented on the behaviour of FeNPs in the landfill leachate in this work can be explained as a combining influence of all the described processes. As evident from Figures 28A1 and 28C1, the mechanism of settling of the NPs in the landfill leachate prevailed. When TMAH was applied for the dispersion of FeONPs (Figure 28B1), the microorganisms, which were present in the tested leachate, most likely used oleic acid as a source of carbon and removed it from the surface of FeONPs (Williams et al, 1947; Corcoran et al., 2007). Thus, the double layer coating was reduced. This enabled the oxidation of FeONPs and the further formation of iron corrosion products, causing their settling under the same mechanisms as described for nZVI and Fe_3O_4NPs. From the comparison of the influences of the particular sample matrix on the behaviour of FeONPs dispersed with TMAH in Milli Q water (Figure 26B1), forest spring water (Figure 27B1) and landfill leachate (Figure 28B1), it can be seen that the most pronounced effects of sample matrix were observed for the landfill leachate.

When mixing was used to disperse FeNPs in the landfill leachate, the effect of the ionic strength prevailed over the influence of dissolved organic matter, leading to the rapid settling of FeNPs (Figures 28A2, 28B2 and 28C2).

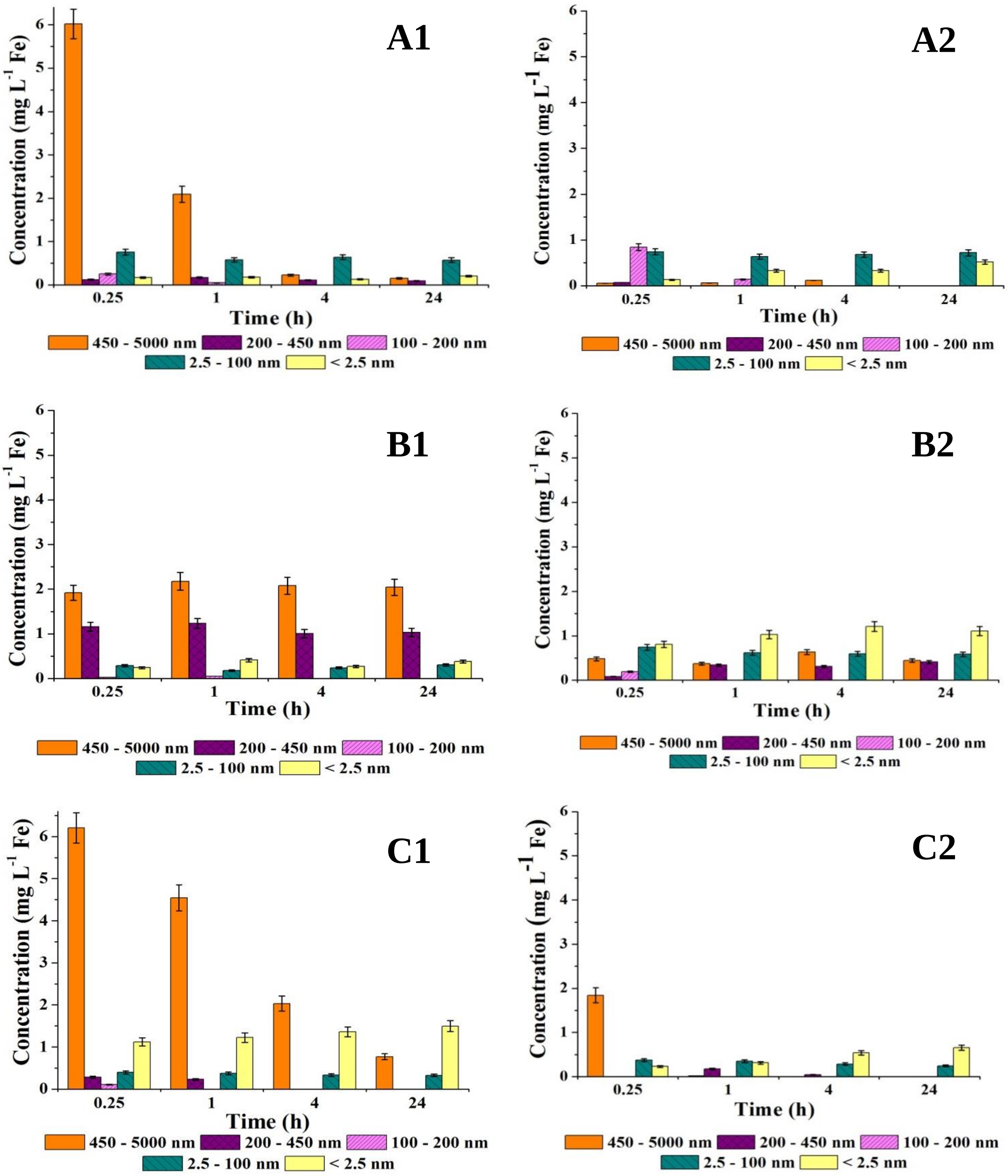

Figure 28: Time dependent size distribution of iron in a landfill leachate treated with nZVI (A), FeONPs (B) and Fe_3O_4NPs (C). The FeNPs (iron load 1.5 g L^{-1}) were dispersed with TMAH (1) or by mixing (2). The concentration of iron in the fractions obtained by the sequential filtration of the samples was determined by ICPMS. The error bars represent the experimental and analytical uncertainty.

5.4.2 Removal of metals from forest spring water and landfill leachates by iron nanoparticles

In the same samples in which the fate of FeNPs was investigated, the efficiency of the removal of potentially toxic elements (Ba, Mn, Al, Cu and V), which were present in measurable concentrations in forest water and landfill leachate was also studied. Ca, as a representative of not toxic metals, was examined as well to find out if FeNPs influence its concentration after the treatment of environmental waters. The samples were analysed 24 h after the treatment. Size distribution of metals in untreated samples and samples treated with FeNPs, using TMAH or mixing for dispersion, was determined by measuring the total metal concentrations with ICPMS. Treatment by FeONPs using mixing for dispersion was not carried out as their hydrophobicity causes their attachment to the walls of the containers, which were used in the experiment. Once attached to the walls, FeONPs are not having any influence on the metal removal. Since FeNPs may contain elements and so can contribute to their occurrence in the water where NPs were added, the concentrations of Ca, Mn, Ba, Al, Cu and V were preliminary determined in Milli Q water.These results are presented in Table 8. It was experimentally verified that TMAH did not contain any of the investigated elements. Their concentrations were below 0.1 μg L^{-1}. In table 9 the pHs of samples before and after the treatment are given.

Table 8: Concentrations of elements in Milli Q water treated with nZVI, FeONPs or Fe_3O_4NPs, dispersed by mixing, 24 h after the treatment with FeNPs. The concentrations of the elements were determined by ICPMS.

Parameter	Ca (mg L^{-1})	Ba (μg L^{-1})	Mn (μg L^{-1})	Al (μg L^{-1})	Cu (μg L^{-1})	V (μg L^{-1})
nZVI (Mixing)	0.63 ± 0.06	176 ± 9	181 ± 9	38 ± 3	26 ± 2	2.8 ± 0.3
nZVI (TMAH)	0.30 ± 0.03	8.7 ± 0.8	50 ± 5	277 ± 7	32 ± 3	3.7 ± 0.7
FeONPs (TMAH)	0.53 ± 0.05	1.6 ± 0.1	0.36 ± 0.032	8.1 ± 0.7	0.13 ± 0.01	< 0.1
Fe_3O_4NPs (Mixing)	1.5 ± 0.1	2.7 ± 0.2	25 ± 2	0.25 ± 0.02	< 0.1	< 0.1
Fe_3O_4NPs (TMAH)	0.33 ± 0.03	0.97 ± 0.09	3.1 ± 0.3	65 ± 5	0.54 ± 0.005	1.3 ± 0.1

Table 9: pH of water samples after the treatment with FeNPS, using TMAH or mixing for dispersion.

Sample	FeNPs	Treatment TMAH	Treatment mixing
Milli Q water	nZVI	13.0 ± 0.1	6.1 ± 0.1
	FeONPs	12.1 ± 0.1	6.1 ± 0.1
	Fe_3O_4NPs	12.9 ± 0.1	6.0 ± 0.1
Forest spring water	nZVI	13.0 ± 0.1	5.9 ± 0.1
	FeONPs	11.9 ± 0.1	6.0 ± 0.1
	Fe_3O_4NPs	13.0 ± 0.1	6.0 ± 0.1
Landfil leachate	nZVI	9.1 ± 0.1	8.0 ± 0.1
	FeONPs	9.1 ± 0.1	7.9 ± 0.1
	Fe_3O_4NPs	8.9 ± 0.1	7.9 ± 0.1

The efficiency of the removal of selected elements from forest spring water by the use of FeNPs is presented in Figure 29.

As it can be seen from the data of Figure 29, the concentration of Ca in untreated forest spring water was 1.5 mg L^{-1}. nZVI and Fe_3O_4NPs dispersed with TMAH were only slightly contaminated with Ca ions (Table 8). A high pH (pH 13) (Table 9) contributes to the co-precipitation of $Ca(OH)_2$ with iron corrosion products and thus, to efficient removal of Ca from forest spring water (Park et al., 2014). Despite the high pH, FeONPs dispersed with TMAH did not remove Ca from the forest water, since the double layer of TMAH and oleic acid prevented the formation of iron precipitate. The concentration of Ca after the treatment with FeONPs was slightly enhanced, due to the Ca content in FeONPs. The removal of Ca from forest water was also not effective by nZVI and Fe_3O_4NPs, when mixing was used for the dispersion. This can be explained by the poor formation of iron corrosion products and $Ca(OH)_2$ at pH 6. The concentration of Ca was increased for the amount corresponding to that arising from the Ca content in the used NPs.

The concentrations of Ba and Mn in forest spring water were low (below 1 μg L^{-1}). Treatment with FeONPs or Fe_3O_4NPs particles, which were not contaminated with Ba and Mn did not influence their concentrations in forest water. Opposite, a high contamination of nZVI particles with Ba and Mn ions (about 170 μg L^{-1}) caused the increase of their concentration in forest water (Table 7). As evident from the data of Figure 29, when mixing was applied for the dispersion of nZVI at pH 6, Ba and Mn were released from the surface of nZVI to the forest water, while, when TMAH is used for dispersion at pH 13, the released contaminants formed hydroxides that were co-precipitated with iron corrosion products.

Al was evenly distributed between different particle sizes with a concentration of about 60 µg L^{-1}. Al chemistry in aqeous samples depends strongly on the pH. At a pH below 5, $Al(H_2O)_6^{3+}$ species prevail. In less acidic solution $Al(H_2O)_6^{3+}$ undergoes hydrolysis to yield $Al(H_2O)_5(OH)^{2+}$ and $Al(H_2O)_4(OH)_2^{+}$ species. At pH 6, $Al(H_2O)_5(OH)^{2+}$, $Al(H_2O)_4(OH)_2^{+}$ and sparingly soluble $Al(OH)_3$ species are present. In the neutral pH range, is Al mainly precipitated as $Al(OH)_3$. By increasing the alkalinity of the sample, at pHs higher than 8, the precipitate starts to re-dissolve, resulting in the progressive formation of $Al(OH)_4^-$ species. Between pH 8 and pH 12, the $Al(OH)_3$ and $Al(OH)_4^-$ species exist, while at a pH higher than 12, highly soluble $Al(OH)_4^-$ is the only Al species present (Ščančar and Milačič, 2006). As can be seen from the data of Tables 8 and 9, when nZVI was dispersed by mixing (pH 6), the soluble Al species were released from the surface of nZVI particles into Milli Q water (Al concentration 38 µg L^{-1}). Application of TMAH for the dispersion of nZVI (pH 13) caused the release of Al from their surface due to the formation of highly soluble $Al(OH)_4^-$ species (Al concentration 277 µg L^{-1}). For similar reasons, but in much lower extent, the Fe_3O_4NPs particles contribute to the contamination of Millli Q water by Al. The behaviour of Al in the forest spring water, which was treated with nZVI or Fe_3O_4NPs, that were both dispersed by the addition of TMAH, followed the phenomena described above. After the treatment, the pH of the forest spring water samples was increased to pH 13 that solubilized the Al originally present in the samples and that one arising from the contamination of the added FeNPs.

As evident from Figure 29, Cu was present in forest spring water in trace amounts (0.5 µg L^{-1}). Consequently, the treatments with FeONPs or Fe_3O_4NPs, which did not contain Cu, have no influence on its concentration in the treated spring water. However, a significant increase of its concentration in forest spring water was observed when water samples were treated with nZVI. The amount of Cu, which was released to the forest water was equal to that released from the surface of nZVI particles in Milli Q water (Table 8).

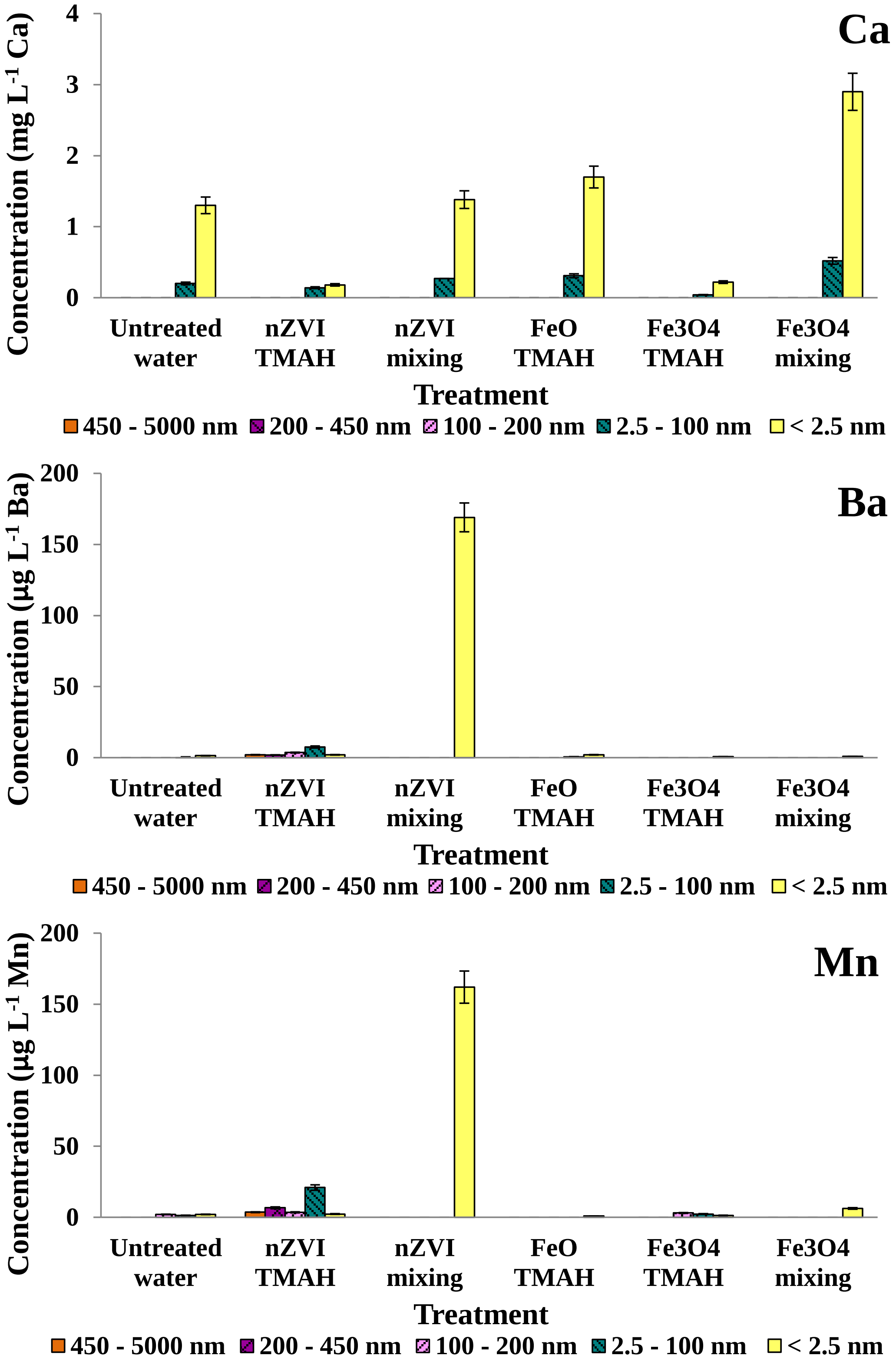

Figure 29: Size distribution of metals in untreated forest spring water and in spring water, 24 h after the treatment with nZVI, FeONPs or Fe$_3$O$_4$NPs. TMAH or mixing was used for the dispersion of the FeNPs. The elements in the fractions obtained by the sequential filtration of the samples were determined by ICPMS. The error bars represent the experimental and analytical uncertainty.

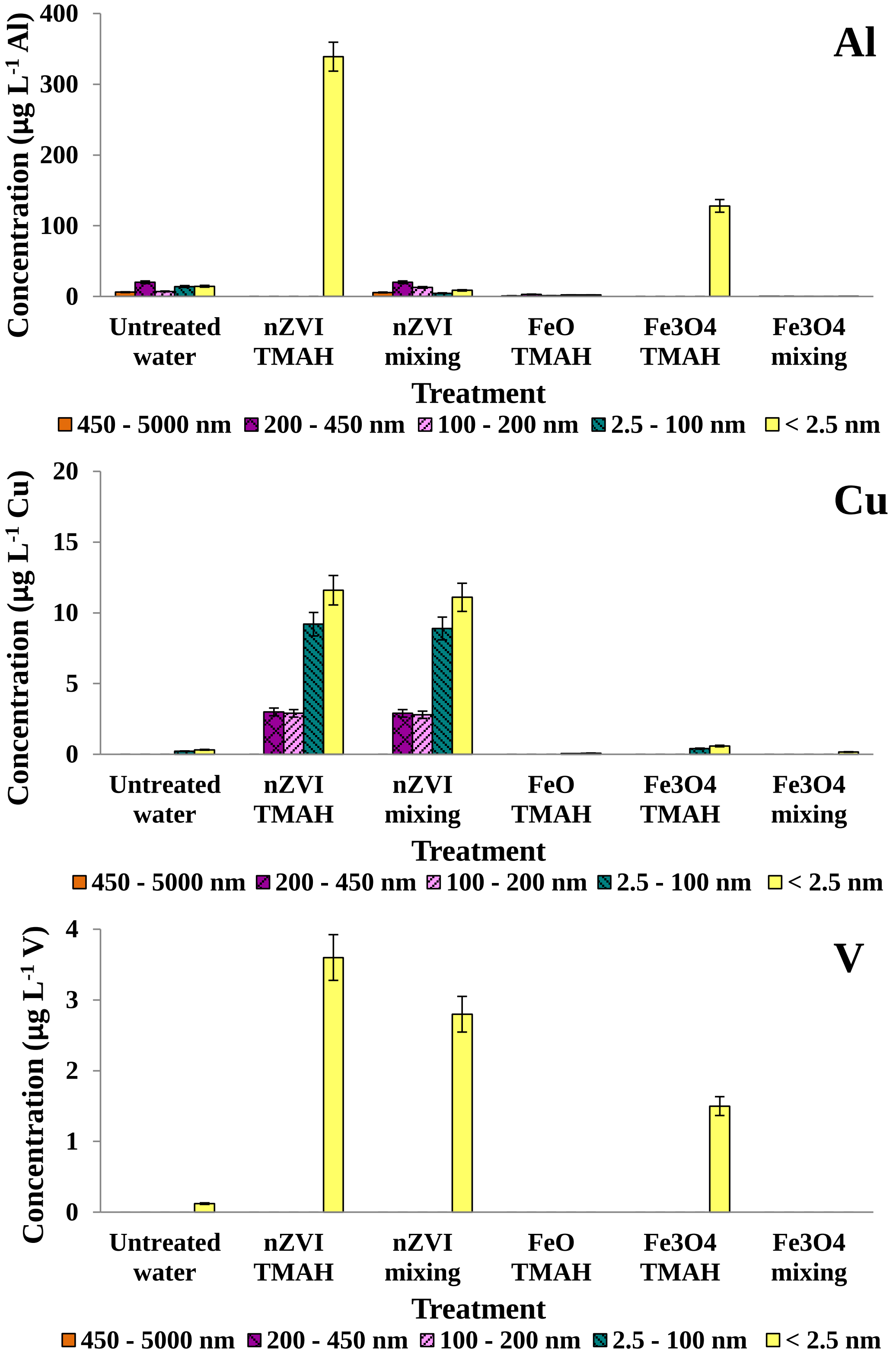

Figure 29 (continued): Size distribution of metals in untreated forest spring water and in spring water, 24 h after the treatment with nZVI, FeONPs or Fe_3O_4NPs. TMAH or mixing was used for the dispersion of the FeNPs. The elements in the fractions obtained by the sequential filtration of the samples were determined by ICPMS. The error bars represent the experimental and analytical uncertainty.

Like Cu, the concentration of V in forest spring water was very low (0.1 μg L^{-1}). Treatment of this water with nZVI (dispersed by mixing or TMAH) or Fe_3O_4NPs (dispersed with TMAH) contributed to the contamination of forest water in amounts between 1 to 4 μg L^{-1}.These amounts corresponded to those of V released to the Milli Q water from the surface of nZVI or Fe_3O_4NPs, respectively (Table 8).

The behaviour of the elements, which were determined in landfill leachate after its treatment with FeNPs was different than that observed in forest spring water. Among all the aqeous samples studied in this work, the leachate samples were characterised by the highest element concentrations, ionic strength, the content of organic matter and pH (pH 8) (Table 7).

The efficiency of the removal of selected elements in landfill leachate by FeNPs is presented in Figure 30. These data indicate that, in untreated landfill leachate, Ca was present in the dissolved form. Its concentration was about 100 mg L^{-1} and was so high that the contamination arising from FeNPs could be considered as negligible. The treatment of leachate with FeNPs dispersed with TMAH increased its pH from 8 to 9. At pH 9, $Ca(OH)_2$ is formed, which is co-precipitated with iron corrosion products. Since the treatment with FeNPs, dispersed by mixing, did not change the pH of the leachate (pH 8), Ca was in this case not co-precipitated and thus, not removed from the solution.

In untreated leachate, Ba and Mn were mainly present in the dissolved form in concentrations of about 250 μg L^{-1} and 150 μg L^{-1}, respectively. The high contamination with Ba and Mn (about 170 μg L^{-1}), arising from nZVI particles (Table 8), is reflected in their remaining concentrations after the leachate treatment. As evident from the data of Figure 29, when mixing was applied to disperse nZVI, only 30% of Ba was removed from the leachate, while the Mn concentration was due to the contamination of nZVI, increased for about two times. A much more effective removal of these two elements is obtained when nZVI is dispersed with TMAH. Namely, at a pH of 9, Ba and Mn ions are more effectively adsorbed on the surface of nZVI and co-precipitated with iron corrosion products. FeONPs and Fe_3O_4NPs, which are not contaminated with Ba and Mn, effectively removed these two elements from the leachate.

In landfill leachate, Al was mainly distributed between the dissolved and nanosized (2.5 - 100 nm) fractions in a concentration of about 185 μg L^{-1}. As can be seen from the data of Figure 30, none of the treatments applied, removed effectively Al from the leachate. The extent of removal depended on the pH, which influences the Al speciation, the dispersion efficiency and the contamination arising from FeNPs.

Cu was present in the landfill leachate in a concentration of 56 µg L^{-1}. It was bound to the coarser particles and was distributed between the 200 - 450 nm and 450 - 5000 nm particle size fractions. After the leachate was treated with FeONPs or Fe_3O_4NPs, which were not contaminated with Cu, the re-distribution from coarser to smaller particle sizes (2.5 - 100 nm and < 2.5 nm) was observed. This indicates that there were interactions of these FeNPs with the particulate matter to which Cu was bound in the leachate. However, the treatment with FeONPs and Fe_3O_4NPs had no influence on the removal of Cu. This phenomenon was most probably related to the strong tendency of Cu to form complexes with available low molecular mass (e.g. citric) and high molecular mass (e.g. fulvic, humic) organic acids present in the leachate (Ščančar et al., 2001). These negatively charged Cu complexes were not adsorbed on the surface of FeNPs due to repulsive forces. Another phenomenon in the behaviour of Cu was also observed after the treatment of the leachate with nZVI. nZVI particles were contaminated with Cu. The Cu concentration, which was released from the surface of nZVI into Milli Q water, was 26 µg L^{-1} or 32 µg L^{-1}, when mixing or TMAH was used for dispersion, respectively (Table 8). After the treatment of landfill leachate with nZVI, strong complexes between organic acids and Cu were formed. This complexation caused the desorption of Cu from the surface of nZVI. As a result, Cu was released into the leachate. Its concentration was increased to about 240 µg L^{-1} and was much higher than that found in the untreated leachate. The treatment of the leachate with nZVI is not efficient for the removal of Cu due to the repulsive forces between the formed negatively charged Cu complexes and nZVI particles, which kept Cu in solution.

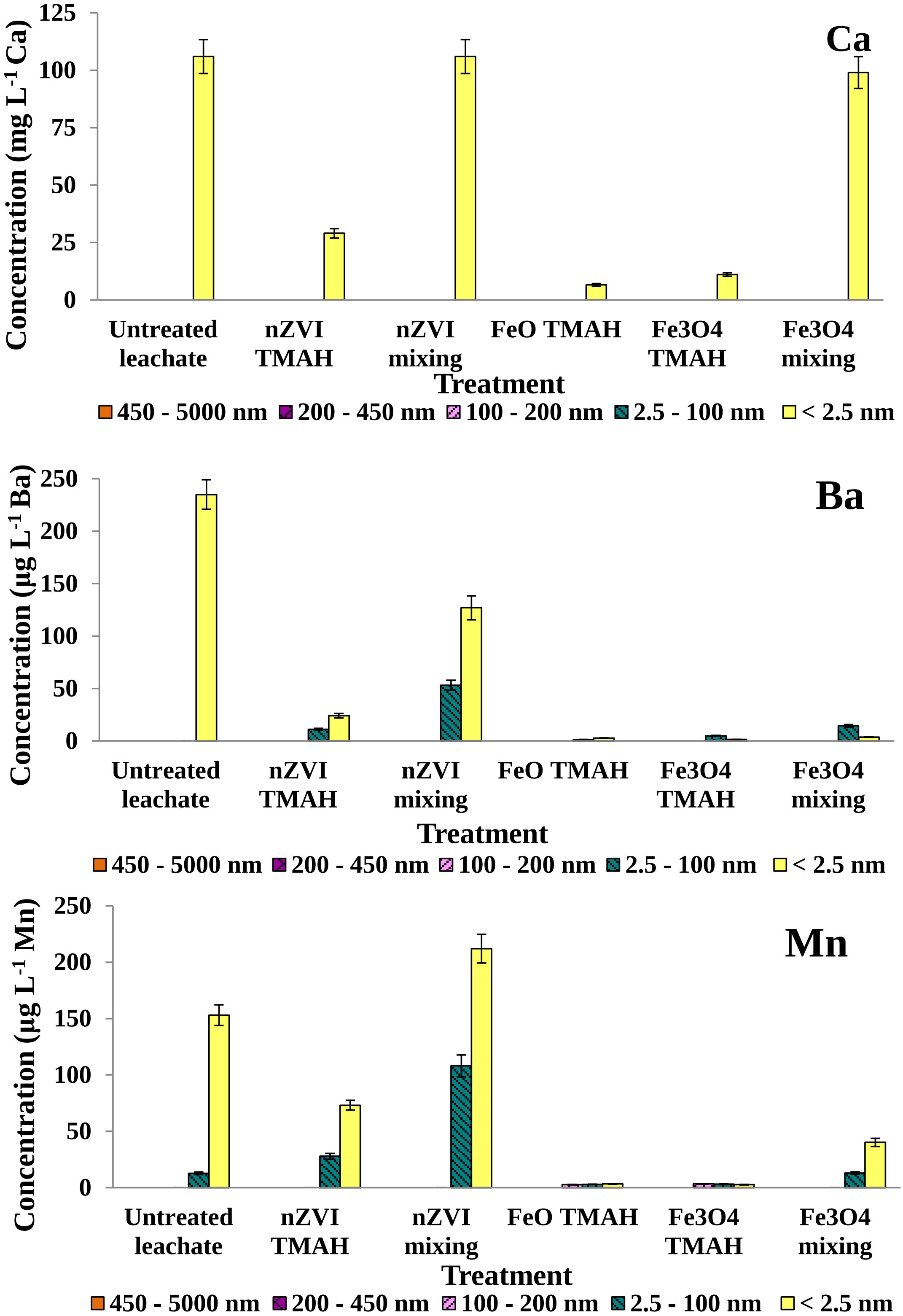

Figure 30: Size distribution of metals in an untreated leachate and in a leachate, 24 h after the treatment with nZVI, FeONPs or Fe_3O_4NPs. TMAH or mixing was used for the dispersion of the FeNPs. The elements in the fractions obtained by the sequential filtration of the samples were determined by ICPMS. The error bars represent the experimental and analytical uncertainty.

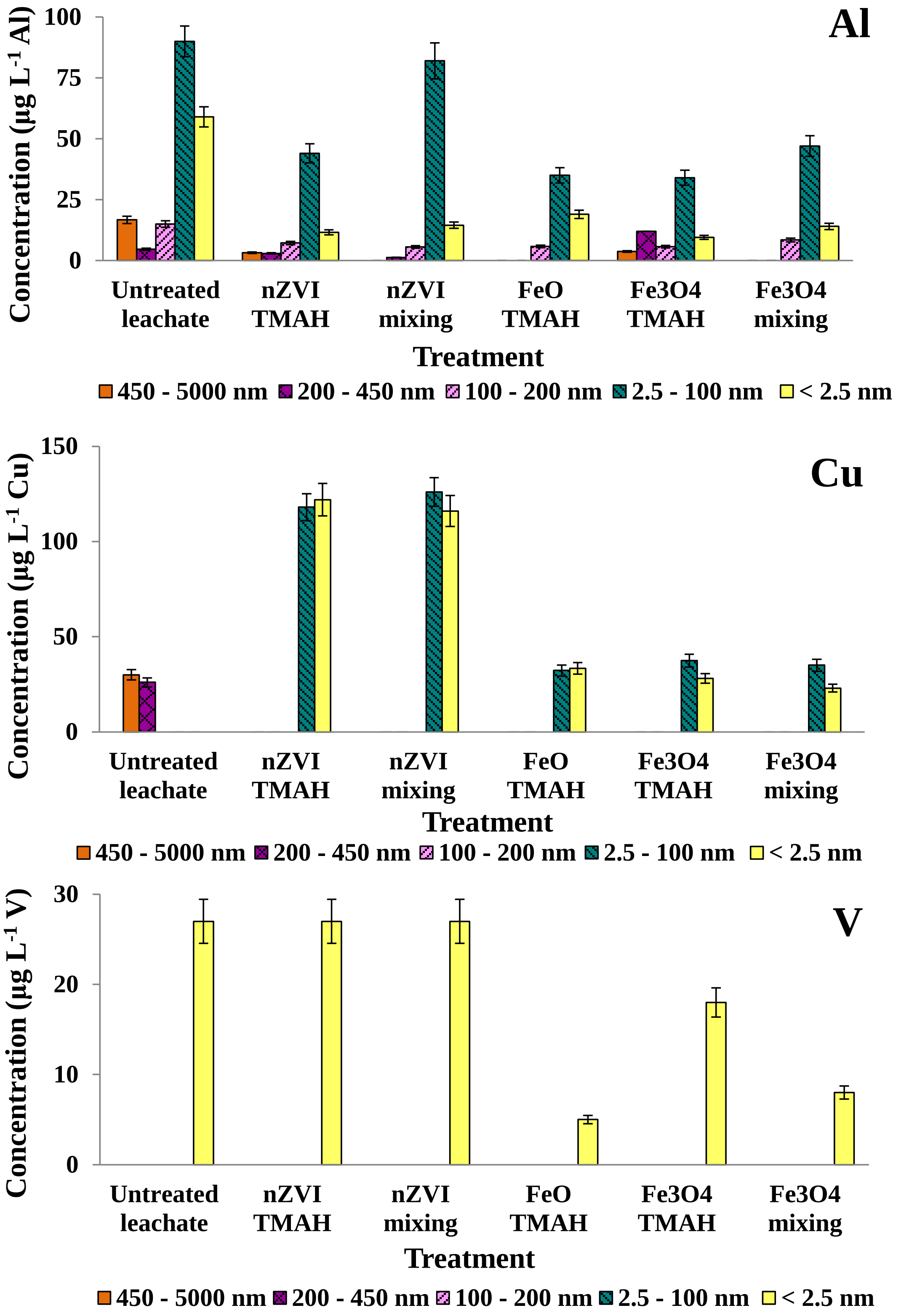

Figure 30 (continued): Size distribution of metals in an untreated leachate and in a leachate, 24 h after the treatment with nZVI, FeONPs or Fe_3O_4NPs. TMAH or mixing was used for the dispersion of the FeNPs. The elements in the fractions obtained by the sequential filtration of the samples were determined by ICPMS. The error bars represent the experimental and analytical uncertainty.

In untreated leachate and in leachate treated with FeNPs, V was present in the dissolved form. Its concentration in the leachate was 27 µg L^{-1}. After the treatment with Fe_3O_4NPs, the extent of the removal of V depended on the pH, which influences the V speciation (Aureli et al., 2008). The more effective dispersion efficiency of FeONPs dispersed with TMAH, in comparison to Fe_3O_4NPs, contributes to a better removal of V from the leachate. When the leachate was treated with nZVI, V present in the sample in oxidation states V^{5+} and V^{4+} was reduced to stable V^{3+} species. V^{3+} readily reacts with available organic ligands and forms negatively charged complexes in neutral up to slightly alkaline pH ranges (Briucal et al., 2004). Repulsive forces between the negatively charged V(III) complexes and nZVI particles, prevented the removal of V from the investigated leachate.

6 CONCLUSIONS

In this doctoral thesis, processes that govern the transformations of toxic OTCs in landfill leachates were investigated by the use of Sn-enriched butyltin and ionic tin tracers. The potential of different FeNPs for the removal of TBT and TMeT from the leachate was studied in order to prevent the release of these toxic pollutants into the environment.

A new procedure was developed for the fast and simple synthesis of ^{117}TBT from ^{117}Sn-enriched metal on a micro-scale. The synthesis starts from only 10 mg of metallic ^{117}Sn. The low mass of the starting material is of crucial importance due to the high costs of the Sn-enriched metal. The main steps of the synthesis comprised bromination of metallic ^{117}Sn, followed by butylation with BuLi. The formed $^{117}SnBu_4$ was then transformed to ^{117}Sn-enriched TBTCl using concentrated HCl. The NMR technique was applied for characterisation of the products during the development of the synthetic procedure. The purity of the synthesised ^{117}TBT was tested by speciation analysis using GC-ICPMS and was found to be 93.5 %, with a synthesis yield of around 60 %. The product was stable for at least six months. The main advantages of the developed procedure are the simplicity, reliability and the reproducibility of the synthesis and its performance at a micro-scale level. Under the developed procedure, ^{117}TBT can be synthesized from ^{117}Sn-enriched metallic tin with a purity that allows its use as a tracer in investigations of the fate of OTCs in environmental compartments, and for the accurate determination of TBT concentrations in environmental samples by ID mass spectrometry.

The transformation of OTCs in landfill leachate was followed over a time span of six months in samples of landfill leachate and in leachate spiked with isotopically enriched tin tracers. The use of isotopically enriched tin tracers allowed the simultaneous observation of the processes of OTC transformation in the leachate itself and of the spiked isotopically enriched tin tracers. To discriminate between the biotic and abiotic transformations of OTCs and inorganic tin species, sterilization of the leachate was also performed and the data were compared to non-sterilized samples. Such an experimental approach provides new insights into the mechanisms of methylation and degradation of OTCs in landfill leachates by the microbial community. Biomethylation processes result in the formation of toxic methyltins, while biodegradation of TBT leads to less toxic tin species. Under landfill conditions, methyltin formation occurred only by biomethylation of inorganic tin. The methylation processes were observed for both, Sn^{2+} and Sn^{4+} ionic species. The hydrolysis of Sn^{2+} and Sn^{4+} species was found to be a limiting factor, controlling the extent of methyltin formation in the landfill leachate. The butyltin concentration was far too low to be degraded into sufficient concentrations of inorganic tin, which could be further methylated by bacteria. The degradation rate of OTCs to inorganic tin is dependent on the carbon energy available for bacteria, which is the highest in tri-substituted OTCs. The degradation process may be inhibited if OTCs are present in concentrations which are toxic to bacteria. Knowledge of the biomethylation pathways and of biotic and abiotic degradation of OTCs in landfill leachates is of significant importance for managers of landfills, assuring their adequate clean-up before the leachates are released into the environment.

The efficiency of the removal of TBT and TMeT from leachates, by the use of nZVI, FeONPs and Fe_3O_4NPs, depended on the conditions under which the remediation procedure was performed. The results from the determination of OTCs in leachate fractions with particle sizes > 5000 nm, 450 - 5000 nm, 2.5 - 450 nm, and < 2.5 nm revealed that TBT was associated to particles bigger than 2.5 nm, while TMeT was present mainly in the fraction with particle sizes less than 2.5 nm. At pH 8, the adsorption of TBT to FeNPs prevailed, while at pH 3 (adjusted with citric acid), the Fenton reaction provoked the degradation of TBT by hydroxyl radicals. In the leachate, spiked with TBT and TMeT (1000 ng L^{-1} Sn), TBT was the most effectively removed (96 %) when a sequential treatment of the leachate with nZVI (dispersed by mixing) was applied, first at pH 8, followed by a nZVI treatment of the aqueous phase, which was previously acidified to pH 3 with citric acid. For TMeT, which is a hardly degradable species, the same treatment was less effective and only about 40 % of TMeT was removed from the leachate. It was proven that TMAH, which is commonly used as a dispersing agent, provoked methylation of ionic tin species. Due to this reason, mixing was recommended for the dispersion of nZVI.

When FeNPs are used for the remediation of surface- and groundwaters, the remaining NPs after the treatment may cause hazardous effects to the environment. The results revealed that the settling and removal of FeNPs from environmental waters depend strongly on the sample characteristics and the ways of nanoparticle dispersion. After the treatment of Milli Q water with nZVI dispersed by mixing or TMAH, a precipitate was formed and nZVI was efficiently removed from the solution within 24 h. FeONPs and Fe_3O_4NPs dispersed by mixing were also effectively removed. However, dispersion with TMAH resulted in the persistence of FeONPs for at least 24 h after the treatment, in the same concentration as was added (1500 mg L^{-1} Fe). The reason of its presistence is the creation of a double layer of oleic acid and TMAH around these NPs, which prevented the formation of iron corrosion products. Fe_3O_4NPs dispersed with TMAH persisted also 24 h after the treatment in solution, but in much lower extent (70 mg L^{-1} Fe). In forest spring water, the ionic strength of the sample contributed to the rapid removal of nZVI, FeONPs and Fe_3O_4NPs. The exception was FeONPs dispersed with TMAH, which persisted for at least 24 h after the treatment in the nanosized form, in the same concentration as was added. In landfill leachate, the high ionic strength of the sample contributed to the efficient removal of nZVI, FeONPs and Fe_3O_4NPs, already 4 h after the FeNPs treatment. Although TMAH is a common surfactant, it is not recommended for being used as a dispersing agent in the treatment of environmental waters by FeNPs, since it is toxic, it can provoke methylation of ionic tin species, and may cause the long-term persistence of FeONPs and Fe_3O_4NPs in aqueous samples with a low ionic strenght. The removal of elements from environmental water samples depends on the contaminant concentration, the type of used FeNPs and the dispersion efficiency. A significant role in the effectiveness of metal removal by FeNPs play the pH, the ionic strength, the content of organic matter, the presence of complexing ligands and the interactions of FeNPs with the sample matrix. The latter sample characteristics influence the chemical speciation of elements. The chemical speciation contributes also importantly to the overall contaminant removal from environmental waters. It should be pointed out that, when the surface of FeNPs is contaminated by a particular metal, this contaminant may be during the NPs treatment released into the water, which is being remediated.

The outcomes of this doctoral thesis resulted in a new procedure for the synthesis of individual Sn-enriched TBT, significantly contributed to new knowledges on the degradation and biomethylation processes of OTCs in landfill leachates, provided novel alternatives for the effective removal of TBT from landfill leachates by the use of FeNPs, and demonstrated the importance of understanding the behaviour and the fate of FeNPs after the treatment of environmental waters.

In the research performed for this Doctoral Dissertation, stable isotopic tracers were used as advanced analytical tools to follow transformations of OTCs and speciated ID-ICP-MS for their accurate quantification. It should be emphasized that the applied analytical methodology required progressive knowledge of ICP-MS and GC and an experienced analyst.

The work is an original and autonomous contribution to the fields of environmental sciences and analytical chemistry and will significantly contribute to the basic research in chemical speciation, rapidly developing nanoremediation procedures and a better understanding of the cycling of OTCs in the terrestrial environment, considering also formation of highly toxic methytin compounds.

Future perspectives are the following:

- To apply FeNPs for remediation of TBT in other landfill leachates from representative sites around Europe.
- To investigate the possibility of remediating TBT in contaminated marine waters by the use of nZVI with different coatings.

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8 APPENDIX

Within the frame of the doctoral thesis, I have published two scientific papers and two manuscripts were sent for publication. I actively participated to several conferences, where I published four papers in the Conference Proceedings and three abstracts in the Book of abstracts.

For the outstanding and excellent presentation of particularly significant innovative scientific research on the occasion of the 6th Jožef Stefan International Postgraduate School Students' Conference, May 20 – 22, 2014, Ljubljana, I was awarded for the best contribution from the field of Ecotechnology.

Original scientific articles

1. Peeters Kelly, Iskra Jernej, Zuliani Tea, Ščančar Janez, Milačič Radmila. The micro-scale synthesis of ^{117}Sn-enriched tributyltin chloride and its characterization by GC-ICP-MS and NMR techniques. *Chemosphere*, 2014, 107, 386-392.
2. Peeters Kelly, Zuliani Tea, Ščančar Janez, Milačič Radmila. The use of isotopically enriched tin tracers to follow the transformation of organotin compounds in landfill leachate. *Water Research*, 2014, 53, 297-309.
3. Peeters Kelly, Lespes Gaëtane, Ščančar Janez, Milačič Radmila. Adsorption and degradation processes of tributyltin and trimethyltin in landfill leachates treated with iron nanoparticles. *Water Research*, 2015, manuscript submitted.
4. Peeters Kelly, Lespes Gaëtane, Zuliani Tea, Ščančar Janez, Milačič Radmila. The fate of iron nanoparticles in environmental waters treated with nanoscale zerovalent iron, FeO and Fe_3O_4. *Water Research*, 2015, manuscript prepared.

Published scientific conference contributions

5. Peeters Kelly, Lespes Gaëtane, Ščančar Janez, Milačič Radmila. Adsorption and degradation of TBT in spiked landfill leachates treated with iron nanoparticles. In Kravanja Zdravko (Ed.), Bogataj Miloš (Ed.), Novak-Pintarič Zorka (Ed.). *Slovenian Chemical Days 2014, Maribor, 11. - 12. September 2014*. Maribor: Faculty of Chemistry and Chemical Technology, 2014, 8 pages

6. Peeters Kelly, Zuliani Tea, Ščančar Janez, Milačič Radmila. Isotopically enriched tin tracers: a powerful tool to study the transformation of organotin compounds in landfill leachate. In: 6th Jožef Stefan International Postgraduate School Students' Conference, 20.-22. 05. 2014, Ljubljana. Trdin Nejc (Ed.), et al. *Proceedings: part 1*. Ljubljana: Jožef Stefan International Postgraduate School 2014, 73-80.
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8. Peeters Kelly, Iskra Jernej, Zuliani Tea, Ščančar Janez, Milačič Radmila. Synthesis of ^{117}Sn enriched tributyltin. In Kravanja Zdravko (Ed.), Brodnjak-Vončina Darinka (Ed.), Bogataj Miloš (Ed.). *Slovenian Chemical Days 2012, Portorož, 12.-14. September 2012*. Maribor: Faculty of Chemistry and Chemical Technology, 2012, 11 pages.

Published scientific conference contribution abstracts

9. Peeters Kelly, Lespes Gaëtane, Ščančar Janez, Milačič Radmila. Adsorption and degradation processes of tributyltin and trimethyltin in spiked landfill leachates treated with iron nanoparticles. European Winter Conference on Plasma Spectrochemistry, 22. - 26. February, 2015, Muenster, Germany. *Book of abstracts and conference program*.
10. Peeters Kelly, Zuliani Tea, Ščančar Janez, Milačič Radmila. Investigation on transformation processes of organotin compounds in landfill leachates with Sn-enriched isotope tracers. In: 8th Young Researchers' Day, 18. February, 2014, Ljubljana. Žunič Vojka (Ed.), et al. *Program and abstract book*. Ljubljana: Jožef Stefan Institute, 2014, p. 50.
11. Peeters Kelly, Iskra Jernej, Zuliani Tea, Ščančar Janez, Milačič Radmila. Synthesis of ^{117}Sn-enriched tributyltin on a micro-scale level. In: 7th Young Researchers' Day, 19 February, 2013, Ljubljana, Slovenia. Lisjak Darja (Ed.), Dušak Peter (Ed.), Kralj Slavko (Ed.). *Program and abstract book*. Ljubljana: Jožef Stefan Institute, 2013, p. 48

Suivi et devenir des organoétains dans des lixiviats de décharge

Résumé: Les organoétains sont parmi les polluants les plus dangereux connus à ce jour à avoir été introduits dans les écosystèmes aquatiques par l'homme. Les lixiviats de décharge sont des sources importantes de ces substances toxiques. Afin de minimiser leur rejet dans l'environnement, il est important de comprendre les transformations que les organoétains subissent dans ces lixiviats et d'appliquer des procédures d'assainissement appropriées.

Cette thèse a eu pour objectifs principaux i) de contribuer à une meilleure connaissance des processus de transformation des organoétains dans les lixiviats de décharge et ii) d'évaluer le potentiel d'élimination des organoétains par des nanoaparticules de fer (FeNPs).

Dans la première partie, les synthèses de TBT enrichi en ^{117}Sn, DBT enrichi en ^{119}Sn, $SnCl_2$ et $SnCl_4$ enrichi en ^{117}Sn, ont été effectuées à partir d'étain métallique enrichi en Sn.

La dégradation et la biométhylation des organoétains dans des lixiviats ont été ensuite suivies pendant six mois, en utilisant des traceurs isotopiques enrichis en Sn. Pour discriminer entre les transformations biotiques et abiotiques des organoétains et de l'étain inorganique, des lixiviats stérilisés et non stérilisés ont été considérés et les concentrations en organoétains, mesurées dans chaque lixiviat, ont été comparées.

Par la suite, les procédés pouvant conduire à l'élimination du TBT et du TMeT présents dans les lixiviats de décharge, par traitement du lixiviat par différents type de FeNPs ont été étudiés. Le TBT est plus efficacement éliminé (96%) lorsque un traitement séquentiel des lixiviats avec nZVI (dispersé par agitation) est appliqué, d'abord par mise en contact à pH 8, puis par traitement de la phase aqueuse avec nZVI acidifiée à pH 3 avec de l'acide citrique.

Enfin, afin de prendre en compte les effets induits par les procédés de traitement par les nanoparticules de fer, leur comportement a été étudié après leur introduction dans des eaux environnementales (eau de source et lixiviat de décharge) différant par leur force ionique et leur contenu de matière organique. L'efficacité de l'élimination des métaux sélectionnés par les FeNPs a également été évaluée. Les nanoparticules ayant des éléments adsorbés à leur surface peuvent contribuer à une contamination du milieu dans lequel elles ont été introduites.

Mots clés : organoétains, lixiviat de décharge, GC-ICPMS, traceurs isotopiques enrichis en Sn, dégradation, méthylation, assainissement, nanoparticules de fer.

Investigations of the fate of organotin compounds in landfill leachates

Abstract: OTCs are among the most hazardous pollutants known so far to have ever been introduced into aquatic ecosystems by man. Landfill leachates are an important pool of these toxic substances. In order to minimise their release to the nearby environment it is important to understand the transformations that OTCs undergo in landfill leachates and to apply appropriate remediation procedures.

This thesis has as main objectives i) to contribute to a better knowledge on transformation processes of OTCs in landfill leachates and ii) to evaluate the potential of OTCs removal by iron nanoparticles (FeNPs).

In the first part, ‘‘In house’’ synthesis of individual ^{117}Sn-enriched TBT, ^{119}Sn-enriched DBT, ^{117}Sn-enriched $SnCl_2$ and ^{117}Sn-enriched $SnCl_4$ was performed, starting from Sn-enriched metallic tin.

Next, the degradation and biomethylation of OTCs in landfill leachates were investigated over a time span of six months, using Sn-enriched isotopic tracers. To discriminate between biotic and abiotic transformations of OTCs and inorganic tin species, sterilized and non-sterilized leachate samples were investigated and the concentrations of OTCs in each sample were compared.

Thereafter, the processes for the removal of TBT and TMeT from landfill leachates by different FeNPs were studied. It was proven that TBT could be the best removed by a sequential treatment procedure by first adding nZVI (dispersed by mixing) at pH 8, and then by treating with nZVI the aqueous phase, which is acidified to pH 3 with citric acid.

Last, to take in account the effects that are induced by treatment procedures with FeNPs, their behaviour was studied after their introduction to environmental waters (forest spring water and landfill leachate), which differ in their ionic strength and the content of organic matter. The efficiency of the removal of selected metals by FeNPs was also evaluated. It was observed that elements which are adsorbed on the surface of FeNPs can contribute to the contamination of the environment in which they are introduced.

Keywords: organotin compounds, landfill leachate, GC-ICPMS, Sn-enriched isotopic tracers, degradation, methylation, remediation, iron nanoparticles.