Organotins in North Sea brown shrimp (Crangon crangon L.) after implementation of the TBT ban

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ABSTRACT

The organotin (OT) compounds tributyltin (TBT) and triphenyltin (TPhT) are potent biocides that have been used ubiquitously in antifouling paints and pesticides since the mid-1970s. These biocides are extremely toxic to marine life, particularly marine gastropod populations. The European Union therefore took measures to reduce the use of TBT-based antifouling paints on ships and ultimately banned these paints in 2003. Despite sufficient data on OT concentrations in marine gastropods, data are scarce for other species such as the North Sea brown shrimp (Crangon crangon), a dominant crustacean species in North Sea inshore benthic communities. The present study provides the first spatial overview of OT concentrations in North Sea brown shrimp. We have compared these data with historical concentrations in shrimp as well as with sediment concentrations. We have also addressed the effect on the shrimp stock and any human health risks associated with the OT concentrations found. TBT and TPhT in shrimp tail muscle ranged from 4 to 124 and from 1 to 24 μg kg⁻¹ DW, respectively. High levels are accumulated in estuarine areas and are clearly related with sediment concentrations (biota-sediment accumulation factor ~10). Levels have decreased approximately 10-fold since the ban took effect, coinciding with a recovery of the shrimp stock after 30 years of gradual regression. Furthermore, the OT levels found in brown shrimp no longer present a human health risk.

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1. Introduction

Organotins (OTs), generally represented by the formula RₓSnL₄₋ₓ contain a tetravalent tin atom (Sn) covalently bound to 1–4 organic substituents (R; e.g., –CH₃, –C₂H₅, –C₆H₅, and –C₆H₅₂) and 1–3 halogen atoms or oxygen- or sulfur-based organic moieties (L; e.g., –Cl, –F, –SR and –OR). Owing to their strong biocidal activity, tributyltin (TBT, (C₆H₅)₃SnL) and triphenyltin (TPhT, (C₆H₅)₂SnL) have been widely used in pest control. TPhT (“fentin”) has been a popular fungicide in potato, sugar beet and hop culture (Hoch, 2001). In 2003, the EU banned the use of fentin because of serious concerns about operator safety and undesired effects on non-target organisms.

Starting in the mid-1970s, TBT was the compound of choice (and to a lesser extent TPhT) in antifouling agents to reduce drag or damage on ship hulls, buoys, fish nets and cages due to the attachment of fouling organisms (e.g., barnacles, algae). At the end of the 1970s, an undesired impact of TBT on the calcification of oyster shells was observed (Alzieu et al., 1982). Soon thereafter, the relationship between TBT and imposex in marine snails was discovered (Smith, 1981). France was the first country to respond by issuing a ban on the application of OT-based antifouling paints on hulls of ships smaller than 25 m in 1982. Similar bans throughout the North Sea countries followed between 1987 and 1991. In 1989, the EU imposed these measures on all Member States through Directive 89/677/EEC. In 2001, the International Maritime Organization (IMO) adopted the ‘International Convention on the Control of Harmful Antifouling Systems’ (AFS Convention), which prohibited the application of OTs as antifouling agents. The AFS Convention entered into force on 17 September 2007 and globally banned OTs on marine vessels starting on 17 September 2008. The EU transposed the AFS Convention into Regulation (EC) 782/2003, which banned the application of organotin on EU-flagged vessels starting on 1 January 2003. That regulation further obliged all ships visiting EU ports from 1 January 2008 onto to be free of OTs or to at least bear a barrier coating. These measures have led to a slow recovery of TBT-sensitive gastropod populations and their TBT-related imposex.
prevalence is decreasing (Morton, 2009; Oliveira et al., 2009; Rodríguez et al., 2009; Sousa et al., 2009).

Brown shrimp (Crangon crangon L.) has a wide geographical distribution, ranging from the Icelandic coast and the White Sea (North-West Russia) to the Moroccan coast and the Black Sea. It dominates the shallow sandy coastal areas of the southern North Sea and the associated estuaries, from northern France to Denmark, where brown shrimp can comprise up to 80% of the total benthic biomass (Bamber and Henderson, 1994; Cattrijse et al., 1997). In the associated benthic ecosystem, C. crangon has a pivotal function; it is both a prominent predator of juvenile fish and smaller invertebrate species (Pihl and Rosenberg, 1984; Wennhage and Gibson, 1998; Hiddink et al., 2002; Wennhage, 2002) and is also crucial prey for economically important fish species such as cod and whiting. C. crangon also has direct economic importance, with an annual catch of almost 40000 tonnes and a third-place ranking in landings.

2. Experimental

2.1. Sample collection

Samples were collected during 1 September–10 November, 2009 during the Dutch, German and Belgian Demersal (Young) Fish Surveys (DFS in the Netherlands, DYFS in Germany and Belgium) performed by the Institute for Marine Resources and Ecosystem Studies (IMARES, Netherlands), Johann Heinrich von Thünen-Institute, Institute of Sea Fisheries (VIT-SF, Germany) and the Institute for Agricultural and Fisheries Research (ILVO, Belgium) (Supplementary Material, Table 1). Samples were immediately frozen to −20 °C at the related institutes prior to transportation to ILVO (Ostend, Belgium) in polystyrene foam insulated containers. Further sample preparation, extraction, clean-up, gas chromatographic (GC) analyses and quality control were done in accordance with the guidance for monitoring of organotin levels in marine biota (Monteyne et al., 2010) and were performed at the marine chemistry lab (MARCHEM) of MUMM in Ostend, which is accredited in accordance with the recognized International Standard ISO/IEC 17025:2005.

2.2. Sample preparation

Shrimp were allowed to thaw overnight, then were peeled and briefly rinsed with ultrapure water to obtain approximately 100 g of tail muscle for each sampling station. Samples were mixed in borosilicate petri dishes using a rotor/stator type homogenizer (Ultraturrax T25 basic, IKA-Labortechnik GmbH, Staufen, Germany), freeze-dried with a Christ LMC-2 (Martin Christ Gefriertrocknungsanlagen GmbH, Osterode am Harz, Germany) lyophilizer and pulverized manually using a porcelain mortar and pestle. The powder was weighed for calculation of dry weight (DW) – wet weight (WW) ratio, and was stored in a desiccator cabinet until analysis.

2.3. Sample extraction and clean-up

The procedure for OT extraction was based on the use of acid reagents in methanol and stirring in hexane. About 1 g of shrimp powder was transferred into an amber 40 mL screw cap vial, and then 15 mL methanol and 7 mL hexane were added. Samples were buffered to pH 5 by adding 3 mL of 4 M sodium acetate. An aliquot of 25 μL of tripropyltin solution (10 μg Sn/g in methanol) was added as recovery standard prior to derivatization for QA/QC purposes to check the ethylation efficiency of TBT. Ethylation was combined with a continuous desorption process by drop-by-drop addition of 4 mL of sodium tetraethyl borate (Sigma–Aldrich, Steinheim, Germany) prepared with deionized water (5%, v/v) to the samples while vigorously stirring. For the degradation of boroxin formed due to the intensive derivation (Smedes et al., 2000), an aliquot of 5 mL of 10 M sodium hydroxide was added to the samples. Finally, the internal standards tetratropyltin (used for quantification) and pentyltetrophenyltin (additional standard for QA/QC purposes) of a concentration of 4 μg Sn/g in hexane were added to the samples, and the phases were separated by centrifugation. The purity of all solvents was appropriate for organic residue analysis. Chlorinated and ethylated OTs were obtained from QUASIMEME (Wageningen, the Netherlands). Internal standard and recovery standard tetratropyltin and tripropyltin chloride were purchased from Schmidt (Amsterdam, the Netherlands). Glassware was washed with 10% hydrochloric acid and rinsed six times with ultrapure water. Custom-made chromatography columns (200 mm × 9 mm ID) were filled with 2 g of Florisil (Merck, Darmstadt, Germany) and 25 mL of hexane was used as the clean-up elution. The extracts were stored at 4 °C until GC analysis.

2.4. Gas chromatographic analysis

A large-volume injection (LVI) technique was developed (Monteyne et al., unpublished protocol). Fifty microliters of sample was injected by an autosampler (Cobibal, CTC Analytics, Italy) at a rate of 1.7 μL s−1 through a Programmed Temperature Vaporizing (PTV) injector (Thermo Electron Corporation, Austin, TX, USA), using a glass sintered liner. The analytic system consisted of a Trace GC (ThermoQuest, Milan, Italy), a 20 m Rtx®-SILMS analytical column (0.25 mm ID) with a 5% phenyl polysilphenylene-siloxane stationary phase (0.25 μm film thickness; Restek, Bellefonte, PA, USA). The oven was preheated to 35 °C and maintained that temperature for 4 min, after which the temperature was increased at the rate of 20 °C min−1 to 120 °C (tamp 1), at a rate of 7 °C min−1 to 150 °C (tamp 2) and finally at a rate of 20 °C min−1 to 300 °C (tamp 3) (5 min hold). A carrier flow of helium of 1.5 mL min−1 was used. The compounds were detected by a Finnigan Trace MS in electron-impact ionization (EI) mode operating in selected ion monitoring (SIM).

2.5. Quality control

Multi-level calibration curves (r² > 0.995) in the linear response interval of the detector were created for quantification. The identification was based on retention times and intensity ratios of 3 monitored ions for quantification. The quality control was performed by regular analysis of procedural blanks, a procedural spike of 100 ng Sn/g, duplo measurements, internal reference material (mussel tissue) and certified reference material (mussel tissue ERM®-CE477). Recovery of MBT, DBT and TBT in ERM®-CE477 was 117 ± 14%, 97 ± 15% and 99 ± 11% (n = 12, 4-year period), respectively. Recovery of TPhT in the procedural spike is 90 ± 15%. Semi-annual internal proficiency test (QUASIMEME) results were also consistently successful. Limits of quantification (LoQ) for TBT and TPhT were 1 μg kg−1 DW. LoQs of monobutyltin (MBT), dibutyltin

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(DBT), monophenyltin (MPhT) and diphenyltin (DPhT) were 10, 10, 3 and 1 µg kg\(^{-1}\) DW, respectively.

All concentration results further used in this article are expressed as µg of organotin ion per kg, expressed on the basis of DW.

2.6. Sediment data and the biota-sediment accumulation factor

Concentrations of OT and other pollutants in the <63 µm sediment fraction and median grain size of the sampling stations in the Westerschelde estuary during 1999–2009 were obtained through online databases of the Belgian Marine Data Centre (BMDC, http://www.mumm.ac.be/datacentre/) and the Dutch Rijkswaterstaat (www.waterbase.nl). Sediment OT concentrations were used to calculate the Biota-Sediment Accumulation Factor (BSAF), a parameter describing bioaccumulation of sediment-associated contaminants into organisms or their tissues (Burkhard, 2009). BSAFs are useful for ecological risk assessments because concentration data are usually available for sediment, in contrast to biota. Depending on the nature of the contaminant, BSAF calculation varies. The heavy-metal BSAF is defined as the ratio of the tissue concentration versus concentration in surface sediment (<63 µm fraction) on the basis of DW (Ankley et al., 1994). When applied to organic compounds (e.g. PCBs), chemical concentrations are normalized for lipid content of the tissue and organic carbon content of the sediment (Ankley et al., 1992). Metal-type BSAFs were derived for TBT, as it accumulates in body tissues in a similar manner similar to heavy metals, i.e., through selective binding to proteins (Kannan et al., 1996; Kim et al., 1996; Tanabe, 1999).

2.7. Tolerable human daily intake (TDI)

Based on the No Observed Adverse Effect Level (NOAEL) of TBT for immunotoxicity in rats, multiplied by a safety factor 1/100, a TDI of 0.25 µg kg\(^{-1}\) body weight has been proposed (Penninks, 1993). The European Food Safety Authority (EFSA) established a group TDI for the sum of DBT, TBT, TPhT and dioctyltin (DOT) to 0.25 µg kg\(^{-1}\) body weight due to the similarity of their immunotoxic properties. Hence, for each sampling station, summed OT concentrations were used to calculate the allowed daily consumption (in kg FW shrimp meat).

2.8. Landings per unit effort (LPUE)

The largest section of the Belgian sea fisheries fleet consists of smaller bottom trawlers (<250 kW engine power) performing daily inshore trips to provide fresh daily shrimp and demersal fish (i.e., flounder, sole, plaice, dab, cod and whiting) to the local ports. Many

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of these local trawlers swap between shrimp (cod-end mesh size /C24 22 mm) and fish gear (cod-end mesh size >65 mm) on a seasonal basis. Landing data associated with both fishing activities reflects the abundance of the target species in the Southern Bight, as they are corrected by the associated fishing effort. Annual LPUEs (in kg fresh weight (FW) /C2 horsepowe /C0 1 /C2 fishing hours /C0 1) for C. cran-gon are calculated and reported annually to the ICES working Group on Crangon Fisheries and Life History (ICES, 2010). Since 1997, the LPUEs of the major shrimp predators (cod and whiting) were derived in a similar manner (see Supplementary Material for LPUE formula and landing and effort data).

3. Results and discussion

3.1. Spatial distribution of OT accumulation in brown shrimp

In the autumn of 2009, TBT and TPhT levels in shrimp ranged from 4 to 124 and from 1 to 24 μg kg /C1 DW, respectively (Fig. 1; Supplementary Material, Table 1). Levels of MRT, DMT, MPhT and DPht were all below the Limits of Quantification (LoQs: 10, 10, 3 and 1 μg kg /C1 DW, respectively) and are not further discussed. In general, offshore OT concentrations are low, but the levels increase near major estuaries (Westerschelde, Rhine-Meuse Delta, Ems-Dollard, Weser and Elbe). Shrimp OT concentrations in the German Bight (GW2-GW10, Fig. 1; Supplementary Material, Table 1) are relatively high and increase with proximity to the Elbe estuary. The German Bight is characterized by a high direct inflow of riverine water from the Weser and Elbe and advection from the rivers Rhine, Meuse and Ems-Dollard through the continental coastal current. In the German Bight, intensive shipping activity and strong tidal shear currents lead to a continuous disturbance of the sediment bed and resuspension of particulate matter, which increases the biological availability of pollutants (Becker et al., 1992).

TPhT concentrations relative to TBT were highest (>50%) in the stations near the Schelde and Ems-Dollard estuaries and within the Oosterschelde estuary (BCS1, BCS2, ES1, NW8, NCS5, GW1), reflecting the large (historic) use of fentin fungicides in (potato) agriculture in the related catchment areas. Lowest OT concentrations were observed inshore in the Southern Wadden Sea near Texel, near-shore at the Northern Wadden islands Sylt and Rømø and offshore at the Southern sandbanks near De Panne.

3.2. Detailed spatial distribution of OT accumulation in brown shrimp in the Westerschelde estuary

In Westerschelde estuary shrimp, TBT concentration increases gradually from 50 μg kg /C1 DW near Vlissingen (WS2) to 124 μg kg /C1 DW upstream of Terneuzen (WS5) (Fig. 1). Further upstream near Hansweert (WS7) the concentration drops to 85 μg kg /C1 DW, and tends to rise again further upstream (107 μg kg /C1 at WS8). A similar spatial pattern in OT concentration in sediment is observed (Fig. 2A) (Monteyne & Roose, data courtesy of BMDC). The lower OT concen-

Fig. 2. (A) TBT and TPhT concentrations (Y-axis, in μg kg /C1 DW) in shrimp meat and sediment along the longitudinal gradient in the Westerschelde estuary (X-axis). (B) CaCO₃ content (Y-axis, in g kg /C1 DW) and the inverse median grain size (Y-axis, inverted, in μm) of the sediment and (C) Sediment mercury content (Y-axis, in μg kg /C1 DW) along the longitudinal gradient (X-axis) in the Westerschelde estuary, showing similar longitudinal patterns as the sediment OT concentrations.

Fig. 3. Temporal trend of <63 μm sediment TBT concentrations (Y-axis, in μg kg /C1 DW) in the Westerschelde lower estuary (Terneuzen-Vlissingen, between WS2-WS6) and mouth (Southern Vlakte van de Raan, roughly near BCS3-WS1) during 1999–2009 (X-axis). TBT concentrations were obtained through the BMDC and Dutch Waterbase (see Supplementary Material Table 3). Concentrations from different sampling locations (see Supplementary Material Fig. 1) were pooled for the lower estuary and mouth. Means, standard deviations and sample sizes are presented for each sampling date. The single measurement (<LoQ) in the Westerschelde mouth in the summer of 2009 is depicted as 1 μg kg /C1 DW.
TBT content (Fig. 3). The exponential regression associated with the Westerschelde exhibits a clear spatial (Fig. 2A) and temporal trend in the sediment. Sediment in the Western Scheldt estuary is strongly subject to tidal variations, the sediment in the Western Scheldt estuary does not tend to accumulate in the same way as other organic pollutants (e.g. benzo-[a]-pyrene, data not shown) but rather accumulates as heavy metals do (e.g. mercury, Fig. 2C). This concurs with the metal-type accumulation of TBT observed in biota (Tanabe, 1999).

For TPhT, a similar trend was clear in the sediment but less clear in shrimp. TPhT concentrations in shrimp increase gradually from 2 to 7.5 μg kg⁻¹ DW for 2003 originate from Willemsen et al. (2004) and Veltman et al. (2006) (see Supplementary Material Table 2). Based on our measurements at the lower Westerschelde estuary to October 2009, the period of shrimp sampling, and to subsequently derive the related BSAFs. Our results indicate an average BSAF of roughly 10 (Table 1), meaning a strong accumulation and probably a poor metabolization of TBT in shrimp. This is consistent with Veltman et al. (2006), who observed high accumulation ratios of TBT and TPhT in C. crangon, and Takahashi et al. (1999), who found a limited metabolization capacity of TBT in Caprellidae (Crustacea; Malacostraca).

<table>
<thead>
<tr>
<th>Location</th>
<th>Date</th>
<th>BSAF</th>
<th>Sediment concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCS3</td>
<td>June 2003</td>
<td>11.5</td>
<td>27.19</td>
</tr>
<tr>
<td>BCS3</td>
<td>Autumn 2009</td>
<td>20.5</td>
<td>1.41</td>
</tr>
<tr>
<td>WS2-WS6</td>
<td>June 2003</td>
<td>12.6</td>
<td>45.80</td>
</tr>
<tr>
<td>WS2-WS6</td>
<td>Autumn 2009</td>
<td>7.8</td>
<td>12.13</td>
</tr>
</tbody>
</table>

<63 μm Sediment TBT concentrations (in μg kg⁻¹ DW) used were calculated based on the exponential regression formula associated with the temporal trends in sediment TBT concentration (Fig. 3). Shrimp meat TBT concentrations (in μg kg⁻¹ DW for 2003 originate from Willemse and Takahashi et al. (1999), who found a limited metabolization capacity of TBT in Caprellidae (Crustacea; Malacostraca).

3.3. Temporal variation of TBT in shrimp and sediment and BSAF in the Westerschelde estuary

A limited amount of data on OT concentrations in C. crangon is available for the Westerschelde and the Southern Bight only (see Supplementary Material Table 2). Based on our measurements at sampling station BCS3 in September 2003 (29 μg kg⁻¹ DW) and the findings of Willemse and Takahashi et al. (2004) near BCS3 in 2003 (368 and 259 μg kg⁻¹ DW), the TBT concentration in shrimp has decreased more than 10-fold in 6 years. Several observations indicate that the associated BSAFs should be based on the TBT concentrations measured in sediment instead of in suspended solids, which contrasts with the findings of Veltman et al. (2006). BSAF content in shrimp exhibits a comparable spatial trend as in sediment (Fig. 2A). In contrast to suspended solids (data not shown), which are strongly subject to tidal variations, the sediment in the Westerschelde exhibits a clear spatial (Fig. 2A) and temporal trend in TBT content (Fig. 3). The exponential regression associated with the temporal trend shows a good fit (R² = 0.93; see Supplementary Material for the associated regression formula). The regression formula was used to extrapolate the decreasing TBT concentration in shrimp from 2009 to 2010 (Table 1, Fig. 4).

For shrimp, a yet unexplained population decline and recovery was apparent in the Southern Bight, similar to the TBT associated fate of several gastropod populations: since the mid-1970s, the annual LPUE gradually declined until 2002 and has recovered quickly since 2007 (Fig. 4). It is striking that the recent resurrection of the brown shrimp population coincides with the ban of TBT and a near 10-fold drop in TBT concentration levels during the time span under consideration. The recovery of the brown shrimp population in the Southern Bight cannot be attributed to a sudden reduction of fishing effort or predation pressure (e.g. by overfishing), as the LPUE of its most important predators (cod and whiting) indicate (Fig. 4). Effects of environmental OT concentrations on the physiology of C. crangon are unknown, but acute laboratory exposure of C. crangon to TBT showed a strong decrease in activity and expression of the ecodystein receptor, a nuclear hormone receptor crucial for the tight orchestration of development, growth and reproduction (Verhaegen et al., 2010, 2011).

3.4. Putative effect on the shrimp stock in the Southern Bight

In brown shrimp, a yet unexplained population decline and recovery was apparent in the Southern Bight, similar to the TBT associated fate of several gastropod populations: since the mid-1970s, the annual LPUE gradually declined until 2002 and has recovered quickly since 2007 (Fig. 4). It is striking that the recent resurrection of the brown shrimp population coincides with the ban of TBT and a near 10-fold drop in TBT concentration levels during the time span under consideration. The recovery of the brown shrimp population in the Southern Bight cannot be attributed to a sudden reduction of fishing effort or predation pressure (e.g. by overfishing), as the LPUE of its most important predators (cod and whiting) indicate (Fig. 4). Effects of environmental OT concentrations on the physiology of C. crangon are unknown, but acute laboratory exposure of C. crangon to TBT showed a strong decrease in activity and expression of the ecodystein receptor, a nuclear hormone receptor crucial for the tight orchestration of development, growth and reproduction (Verhaegen et al., 2010, 2011).

Adult C. crangon (and other decapods) are believed to be fairly resistant to organotin exposure, with a 96-h-LC₅₀ of 28.5–41 μg L⁻¹ TBTO (Champ, 1986; Verhaegen et al., 2011). Sub-toxic but nonetheless detrimental effects may occur at much lower levels. In the closely related fiddler crab, Uca pugilator, 0.5 μg L⁻¹ was sufficient to significantly disrupt limb generation (Weis et al., 1987). In contrast to adult C. crangon, larval stages are believed to be sensitive towards organotins, with a 96-h-LC₅₀ of 1.5 μg L⁻¹ TBTO: Champ, 1986). In the closely related American lobster, Homarus americanus, 1 μg L⁻¹ TBTO was sufficient to almost completely stop larval growth (Laughlin and French, 1980). Two major issues hamper the demonstration of an unarguable causative link between decreased OT concentrations and the shrimp stock recovery. First, we cannot estimate the historical environmental effects of OTs on larval C. crangon, as fundamental environmental concentration data in larval (planktonic) stages of C. crangon or even of related species are lacking. Second, subtoxic dose-dependent physiological effect data is lacking as the poor survival of larvae, juveniles and adults of C. crangon under laboratory conditions currently hinders reliable
chronic exposure experiments. Once an acceptable adult labora-
tory survival is reached, analysis of hatching success and of early
larval growth and survival after maternal exposure to historical
sediment (or pore-water) OT concentrations could be the key.

3.5. Consumer health risk

In our experiments, the DW to FW ratio of peeled shrimp was
determined at 22.4 ± 1.1% (n = 46). According to the TDI set by EFSA,
a person weighing 60 kg is allowed to consume 5.22 ± 2.86 kg on a
daily basis (n = 35; Supplementary Material, Table 1) of FW shrimp
meat from commercially exploited shrimp areas (excluding the in-
er Ems-Dollard estuary, Oosterschelde and Westerschelde). This
renders brown shrimp a healthy seafood product, in contrast to
its status less than a decade ago. In 2003, the daily consumption
of 169 g of peeled shrimp was sufficient to exceed the TDI for TBT
alone. According to Avia et al. (2011), the average daily consump-
tion of C. crangon meat in Germany and Belgium is estimated at
0.063 g and 1.4 g per person, respectively. These numbers may
not be appropriate for both countries, as a large part of especially
the German population are virtually non-consumers, but it can be
concluded that even people consuming brown shrimp on a daily
basis can do so with no health risks with respect to OT intake.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found,

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