OCCURRENCE OF LEGACY AND EMERGING PERSISTENT ORGANIC POLLUTANTS AT ROSS SEA AND CIRCUMPOLAR DEEP WATER CONVERGENCE (ANTARCTICA)

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Introduction

Persistent organic pollutants (POPs) have attracted the attention of scientists and policy makers in recent decades due to their extreme persistence, semi-volatility, capacity to bio-accumulate in the food chain, and toxic properties. Despite its geographical isolation, extreme meteorological conditions and an almost total absence of local point sources, the Antarctic continent is vulnerable to contamination by POPs, due to the ability of these chemicals to undergo long range atmospheric transport (LRAT) and deposition in the open sea. In a few cases and for limited areas, POPs may be also introduced into the Antarctic ecosystem by human activities (scientific stations, fishing, tourism, accidental oil pills, waste incineration and sewage).

Even if various studies[i.e.1,2,3,4,5] have revealed the presence of POPs in air, seawater, sediments and biota in Antarctica, more investigations are needed to implement the number of observations, integrate the data series and meet the indications of the Stockholm Convention and the UNECE protocol in terms of improving knowledge of the temporal and spatial trends of POPs in biotic and abiotic environmental compartments.

In this study we present POP concentrations in water samples collected along vertical water columns from seven oceanographic stations located in the Ross Sea and close to the Circumpolar Convergence (see Figure 1).

Moreover, the occurrence of emerging and legacy POPs, including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated naphthalenes (PCNs), organochlorine pesticides (OCPs) and polybrominated diphenylethers (PBDEs) were investigated in order to evaluate their possible sources and relationship with physical and biological processes taking place in the water column.

The Ross sea is the formation site of two shelf waters which constitute an important part of the Antarctic Bottom Water (AABWs): the High Salinity Shelf Water (HSSW), which is relatively cold and generated inside the Ross Sea basin and the Ice Shelf Water (ISW). The Ross sea is influenced by only one water mass of external origin, the Circumpolar Deep Water (CDW), which is the largest circulation feature of the Southern Ocean, manly responsible for possible exchange processes between the Antarctic seas and the outer oceans, and thus a possible source of persistent organic pollutants (POPs)[2].

The CDW is a relatively warm, salty and nutrient rich water mass carried around Antarctica by the Antarctic Circumpolar Current (ACC)[6]. Associated with the ACC is the Antarctic Convergence where the cold Antarctic waters meet the warmer waters of the subantarctic creating a zone of upwelling nutrients. Moreover, the Drygalski Glacie Tongue plays an important role in the Polynya development in the Terra Nova Bay, in the Ross sea.

An important environmental concern is the accelerated glacier and snow melting that represent a massive release of both naturally occurring chemical substances and organic/inorganic pollutants of anthropogenic origin, which are stored in the deeper layers of the ice and may be delivered to surrounding ecosystems.

Materials and methods

In the framework of the Italian National Program for Antarctic Research (PNRA), an oceanographic cruise (XXVII Italian Antarctic Expedition) was carried out between January and February 2012 and conducted on board the M/N Italica. Sea water samples were collected at different depths at each station; samplings were performed from a starting depth of at least 5 m to the bottom.

A “Go-flo” stainless steel system for off-shore sampling was used to collect the sea water samples.

The analytical procedures for POPs determination in seawater samples have been described elsewhere[3,7,8]. Briefly, seawater samples were extracted with n-hexane immediately after sampling in the analytical laboratory

onboard the ice-breaker by a high efficiency liquid–liquid extraction system[9]. The organic extracts were sent to the laboratory in Italy for clean-up and instrumental analysis. Immediately before the analysis the organic extract was cleaned-up, concentrated at a suitable volume under a mild nitrogen flow and, finally, analysed by gas chromatography/mass spectrometry. A gas chromatograph mod. 6890A (Agilent, USA) coupled with a mass spectrometric detector mod. 5973A (Agilent, USA), operating both in EI and NCI mode, was used to determine POP concentrations.

In order to minimize and quantify possible sampling and measurements errors, field and laboratory blanks, surrogate recoveries, standard spike recoveries and detection limits procedures were carried out. Water field blanks were performed on highly purified water (40 L) and extracted with the same procedure of the field samples. CTD measurements were also performed in order to determine physical and physico-chemical parameters such as fluorescence, salinity, temperature and to reveal what kind of water masses were present in the investigated vertical water columns.

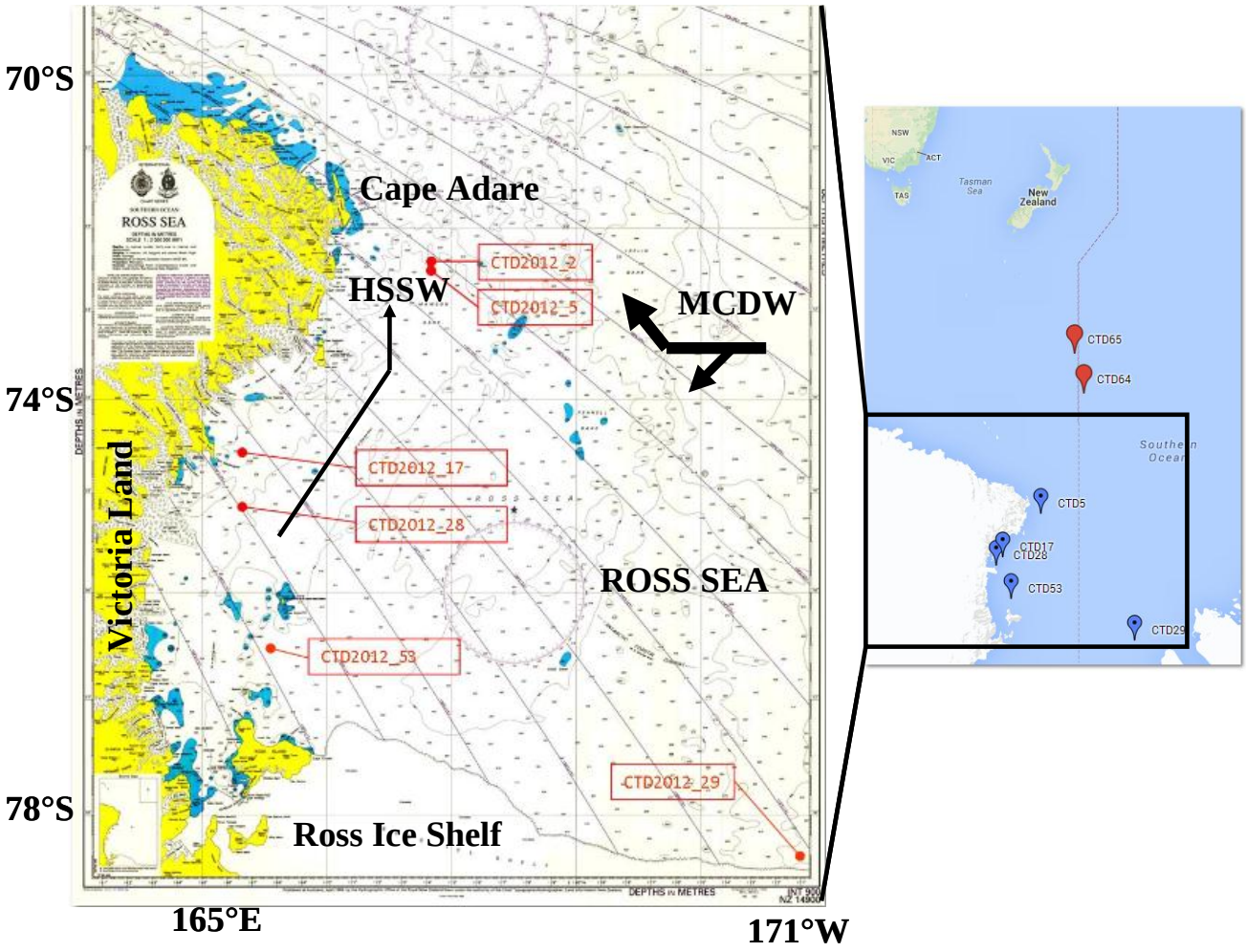

Figure 1
Location of seawater sampling stations.

Results and discussion

Combustion processes and accidental spillages represent the major source of pollution in the Antarctic environment, whose removal by natural degradation processes is slowed down due to low temperatures[10]. The presence of PAHs has been investigated in a large area of the Ross Sea by collecting surface seawater samples during previous Italian Antarctic expeditions. The total content of PAHs in surface sea water samples measured in this study varied between about 4 and 9 ng L^{-1} (see Table 1), showing concentrations values similar or slightly higher than those found during previous expeditions in the same area[2,3,11].

Table 1

Sampling dates and PAHs concentrations (ng/L) for surface sea-water samples collected between January and February 2012 in the Ross Sea.

Site	Sampling date	Latitude	Longitude	Σ PAHs ng/L
CTD2012_2	**01/26/2012**	**72°23.561' S**	**172° 58.196' E**	**5,9**
CTD2012_5	**01/27/2012**	**72°24.570' S**	**172° 58.932' E**	**9,4**
CTD2012_17	**02/01/2012**	**74°42.847' S**	**165° 43.930' E**	**4,1**
CTD2012_28	**02/02/2012**	**75°07.940' S**	**164° 33.623' E**	**5,2**
CTD2012_29	**02/04/2012**	**78°23.6953' S**	**169°11.400' W**	**5,8**
CTD2012_53	**02/08/2012**	**76°39.952' S**	**167°18.434' E**	**5,8**
CTD2012_64	**02/15/2012**	**64°00.4997' S**	**179°00.367' E**	**3,9**
CTD2012_65	**02/16/2012**	**60°28.2299' S**	**179°15.990' E**	**2,9**

The sources of PAHs, either from petrogenic and pyrolytic origin, may be identified by ratios of specific PAH compounds. A ratio between low molecular weight (LMW), two or three rings, and high molecular weight (HMW), four to six rings, higher than 1, dominate in the petrogenic origin[12].

The LMW/HMW ratios in our samples, in particular in the surface samples, seem suggest a predominant petrogenic source.

The temperature and salinity profiles showed distinct differences between the oceanographic stations, evidencing the presence of different water masses. These water masses seemed to affect the distribution of PAHs with depth, in particular in the depths where the intrusion of the relatively warmer MCDW in the colder HSSW was evident (sites CTD02 and CTD05, close to Cape Adare).

PBDEs were also found in seawater at pg L^{-1} levels. BDE209 and BDE47 were the major congeners in all samples collecetd in the Ross sea. The presence of BDE209, which has limited environmental mobility, seemed to suggest inputs from local sources. In fact, sea water samples (CTD64 and CTD65) collected in the Circumpolar convergence area showed the lower PBDE concentration and the absence of BDE209.

Looking at distribution of PBDE with depth, no clear trend could be identified, but it was evident that higher concentration values were found in the sea surface samples.

Among organochlorine pesticides, hexachlorobenzene was detected with concentrations ranging from about 1 to 10 pg L^{-1}. These values were similar to those found in water samples collected in the Ross sea during the austral summer 2003-2004[12]. The HCHs were also the organochlorine pesticides routinely detected in the Antarctic seawater samples. Their higher concentrations levels may be due to the influx from melting sea-ice/snow (i.e.sea water sample collected close to the Drygaslki Glacier) or the presence of warmer water masses.

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