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Poison, plants and Palaeolithic hunters. An analytical method to investigate the presence of plant poison on archaeological artefacts

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ABSTRACT

In this paper we present the development of a method for the detection of toxic substances on ancient arrow points. The aim is to go back in time until the Palaeolithic period in order to determine if poisonous substances were used to enhance the hunting weapons.

The ethnographic documentation demonstrates that hunters of every latitude poisoned their weapons with toxic substances derived from plants and occasionally from animals. This highlights that often the weapons would be rather ineffective if the tips were not poisoned. The fact that toxic substances were available and the benefits arising from their application on throwing weapons, suggests that this practice could be widespread also among prehistoric hunters.

The project reviewed the research of the toxic molecules starting from current information on modern plants and working backwards through the ages with the study of ethnographic and historical weapons. This knowledge was then applied to the archaeological material collected from International museum collections.

Results have shown that using this method it is possible to detect traces of toxic molecules with mass spectrometry (MS) and hyphenated chromatographic techniques even on samples older than one hundred years, which we consider a positive incentive to continue studying plant poisons on ancient hunting tools.

1. Introduction

Within Palaeolithic studies, many questions concerning hunting weapons and the efficiency of the spears/arrows enhanced with stone armatures or bone elements remain unanswered. Recently, use-wear analysis and experimental archaeology have provided new insights into the use and effectiveness of hunting weapons, and now archaeological science methods may help us to further reconstruct the kinds of hunting techniques used during the Palaeolithic period. It may also allow an understanding of the role spears/arrows played in these pursuits (Allchin, 1966; Stanley et al., 1974; Gramly, 1976; Keeley, 1996; Costamagno, 1999; Gaudzinski and Roebroeks, 2000; Lombard, 2005; Shea, 2006; Lombard and Pargeter, 2008; Backwell et al., 2008; d'Errico et al., 2012a,b).

An aspect of prehistoric hunting weapons that was scarcely taken into account by researchers is concerning the use of poisonous substances on arrows.

During the Palaeolithic age, the improvement of the technique of hunting at a distance, with the invention of the throwing weapons (spearthrower, bow), was a real revolution in hunting strategies brought by Modern Humans.

Killing at a distance requires no more a physical confrontation but the use of a "strategy of deceit", which is deeply linked to our species. The deceit lies in the phases of the hunt: the silence of the ambush, the attention to every movement and wind direction, the simulation to allow the approach, and finally the launch and the capture of the prey (Brizzi, 2005).

The "coward's weapon", as the English playwright John Fletcher defined the poisons, is a further deceit that Man uses against the prey, so that it is immediately incapacitated.

The ethnographic documentation teaches us that hunters of every latitude poison their weapons with toxic substances derived from plants and animals (Heizer, 1938; Bisset and Hylands, 1977;

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Bisset, 1979, 1981, 1989, 1992a; Cassels, 1985; Noli, 1993; Neuwinger, 1996; Osborn, 2004; Philippe and Angenot, 2005; Mayor, 2008; Jones, 2009).

A study on the arrows currently used by the Bushmen (Noli, 1993) has highlighted that these weapons would be often ineffective if the tips were not poisoned. The arrows of many hunters, thrown with bows, penetrate into the prey to a depth that is not enough to kill a large animal.

It is not clear to what extent, but Prehistoric populations were familiar with the environment in which where they lived: they knew the edible plants (therefore the toxic ones) and perhaps also their medicinal use. The fact that toxic substances were available to the Prehistoric hunters and the notable benefits arising from their application for hunting (safety distance of the hunter from the prey, quick killing of big prey), suggests that this practice could have been widespread. In particular, the toxic substances may allow for incapacitation of the animal which means that it is not possible to run far away, irrespective of whether a mortal wound was imposed: this is essential for the recovery of meat and skin in good condition.

Formulation of a poison for hunting is relatively easy and the risk is minimal. In modern hunter–gatherer populations poisons are always made by an expert and the substance is conserved in a protected place: for this reason, the poisoning of other members of the group is unlikely.

Taking into account each of these factors, was developed a method capable of detecting plant poisons on archaeological spears/arrows. The main aim was to establish when poisonous substances began to be used in conjunction with weapons as a way of further improving their hunting success.

2. A brief history on the use of poison in hunting

The use of poisoning arrows in Prehistory is yet to be fully proved, as the only study that we have currently has been widely debated.

The debate relates to a wooden stick 32 cm long found in Border Cave, South Africa and dated about 24,500 BP (d'Errico et al., 2012a,b).

The results from gas chromatography analysis carried out on the stick, absolutely similar to the poison applicators used by Kalahari San, indicated traces of ricinoleic acid (castor oil, *Ricinus Communis*). The use of this substance as a poison has been questioned (Evans, 2012; d'Errico et al., 2012a,b) as castor oil is only slightly toxic (if not purified) and not commonly used as a poison. Ricin can be extremely lethal only if purified with modern techniques, and for this reason has been listed as a warfare biological weapon and involved in a number of incidents: the homicide of the dissident Bulgarian Georgi Markov in 1978 is the most famous (Fredriksson et al. 2005; Carrico, 2009; Shep et al., 2009). The lethal dose of castor oil is therefore probably too high to be considered as a poisonous substance for arrow points, also considering that poisons are chosen not only for an immediate action on the nervous or cardiovascular system of the animal, but also to slow their escape. Another weak point of the hypothesis of d'Errico and co-authors is the fact that we have not found any ethnographic comparison for the use of castor oil as a poison on arrows (Bradfield et al., 2015). This does not mean that the primary function of the stick analysed by d'Errico et al., was inevitably different: another component, more toxic, of the compound, could have been lost or not identified. The lump of organic material containing *Euphorbia tirucalli,* found

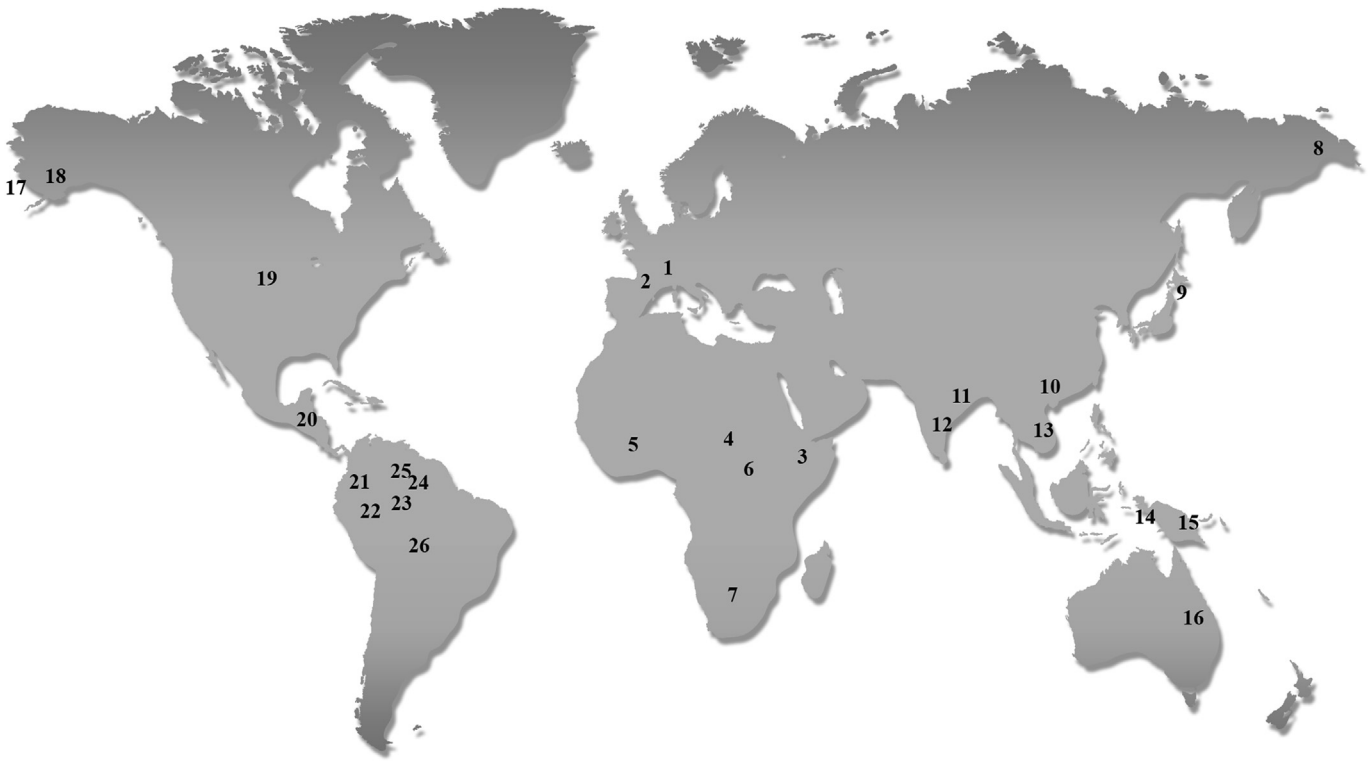

Fig. 1. Map of the principal arrow and dart poison (Bisset, 1989). 1 – Aconitum, 2 – Veratrum, 3 – Acokanthera, 4 – Strophanthus, Physostigma, Erythrophloeum, 5 – Mansonia, 6 – Strychnos, Erythrophloeum, Strophantus, 7 – Diamphidia, Urginea, Adenium, Boophone, 8 – Aconitum, 9 – Aconitum, Dasyatis, Daphne, Cynanchum, Juglans, 10 – Aconitum, Croton, 11 – Strychnos, Alstonia, Abrus, 13 – Antiaris, Strychnos, Lophopetalum, Beaumontia, Strophantus, 14 – Microbial, 15 – Microbial, 16 – Excoecaria? 17 – Palythoa toxica, 18 – Aconitum, 19 – Rattlesnake, Yucca, 20 – Hippomane, Hura, Colliguaja, Euphorbia, Sapium, Sebastiania, Schoenobiblus, 21 – Phyllobates, Naucleopsis, 22 – Naucleopsis, 23 – Chondrodendron/Curarea, 24 – Chondrodendron/Curarea, Strychnos, 25 – Strychnos, 26 – Strychnos.

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