Fig. 4 The calculated northern limits of the path of totality of the 1715 eclipse in relation to Darrington and Badsworth. The limits have the same significance as in Fig. 3.

underestimated the effects of the optical imperfections on the image size in the telescopes used by Picard and La Hire, as argued recently by O'Dell and Van Helden[9].

We thank David Calvert of the Royal Greenwich Observatory for the photographic reproduction of pages 256 and 257 of the *Philosophical Transactions of The Royal Society* for 1715. We are grateful to the Ordnance Survey for their kind permission to reproduce sections of the 1:50 000 maps shown in Figs 3 and 4.

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Entrainment of trace-metal-enriched Atlantic-shelf water in the inflow to the Mediterranean Sea

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Surface waters of the Mediterranean Sea have higher trace-metal concentrations than open Atlantic surface waters[1]. This observation could be explained by sources within the basin, but recent data from the Alboran Sea[2] indicate that trace metals may already be enriched in Atlantic waters flowing into the Mediterranean through the Strait of Gibraltar. Here we present new data documenting the presence of trace-metal-enriched source waters west of the Strait, and present a mathematical analysis showing that Cu, Ni, Cd and Zn distributions in the Alboran Sea can be explained as linear mixtures of four well-defined sources: (1) Spanish coastal
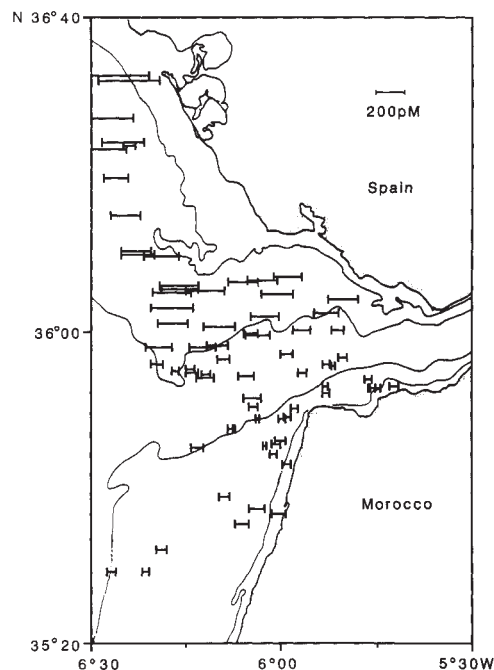
Fig. 1 Surface Cd concentrations during a survey (March–April 1986) of the eastern Atlantic and the Strait of Gibraltar. Station locations are centred on horizontal bars. Length of bar is proportional to Cd concentration. Bathymetry contours at 30 and 200 m.

waters, (2) North Atlantic Central Water, (3) Atlantic surface water, and (4) Mediterranean Levantine Intermediate Water. In this analysis, salinity and trace metals are used for the first time to deconvolve mixing between water masses of different origins.

Chemical budgets for the Mediterranean are influenced by vigorous exchange of Atlantic surface water for deep Mediterranean water through the Strait of Gibraltar. Fluxes through the Strait are 30 times higher than fresh-water inflow to the Mediterranean[3]. Nevertheless, surface Cu, Ni, Cd and Zn concentrations in the Mediterranean are higher than nutrient-depleted Atlantic surface water by up to 2, 2, 9 and 40 times respectively (refs 1, 2 and R. M. Sherrell and E.B., unpublished). If typical Atlantic surface waters were representative of the inflow, this difference would have to be maintained by inputs within the Mediterranean basin. As trace-metal enrichments are present in the inflowing plume[2], sources within the basin may not account for all of the enrichment. Here we show that trace-metal fluxes through the Strait of Gibraltar are enhanced by contributions from two trace-metal-enriched Atlantic sources: (1) Spanish shelf water and (2) subsurface open ocean water. Calculated average Cu, Cd and Zn concentrations of the inflow resemble the actual metal composition of Mediterranean waters for these metals. Therefore the net input of Cu, Cd and Zn within the basin may be dominated by external rather than internal sources.
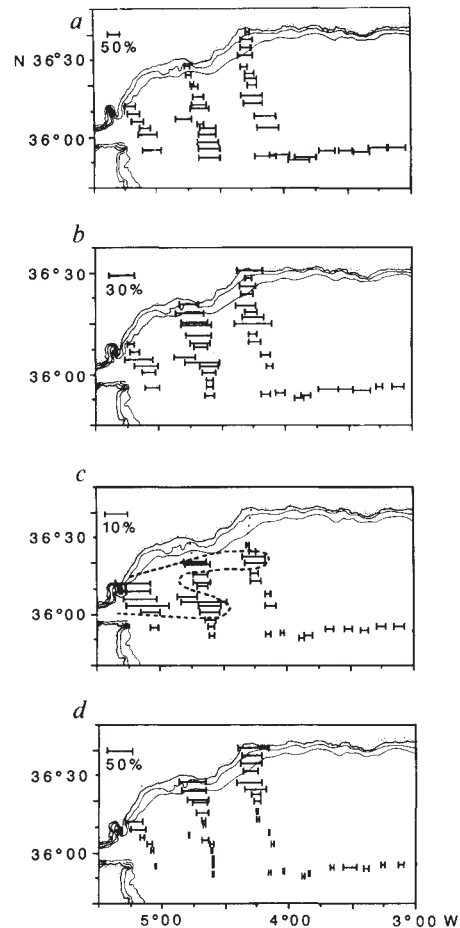
There are two metal-rich water masses to the west of the Strait of Gibraltar. Previous work[2,4] has shown that subsurface Atlantic waters in that region are enriched in Cd, Ni and Zn. Data from other parts of the ocean also show this deep enrichment, which is attributed to the decomposition of metal-rich biological debris at depth. Here we identify a second enriched water mass by collecting many surface samples from the eastern Atlantic on board USNS *Lynch* (26 March – 19 April 1986) and on RV *Oceanus* cruise 176 (14–16 April 1986); Fig. 1 shows surface sampling locations. Samples were collected with a contamination-free underway pumping apparatus, pre-concentrated in the laboratory by modified Co-APDC (cobalt-ammonium pyrrolidinedithiocarbamate) co-precipitation[5], and analysed by graphite furnace flameless atomic absorption. Cd is enriched in Atlantic surface waters on the Spanish shelf outside the Strait
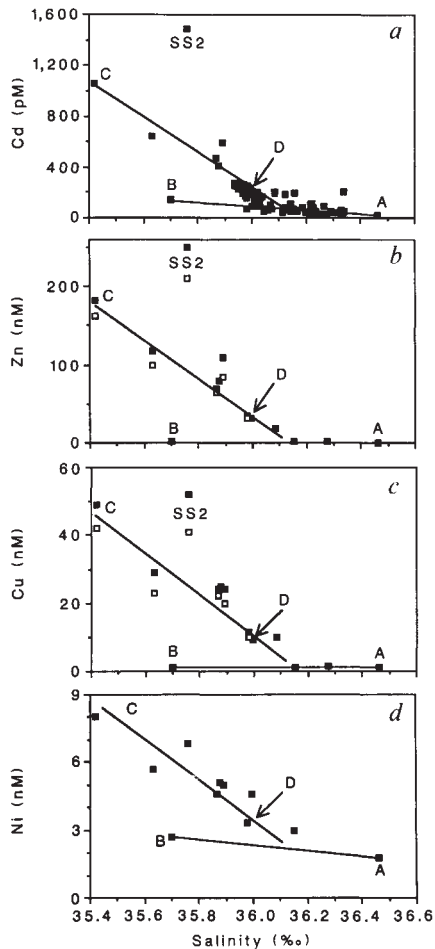
Fig. 2 Metal–salinity correlation in surface samples from Fig. 1. ■, Unfiltered samples; □, filtered through 0.4 μm Nuclepore filter. Atlantic profile end-members are indicated by A (surface) and B (400 m deep). By definition, samples resulting from conservative mixing of these two end-members fall on line segment AB. Positive deviations from this relationship which follow line segment CD are due to a shelf-specific trace-metal enrichment process. Arrow at D indicates metal composition chosen for representative shelf end-member. SS2 deviates from shelf–salinity line owing to variability in these waters. Consistent inter-element ratios argue against contamination.

Fig. 3 End-member fractions in surface samples of the Alboran Sea east of the Strait of Gibraltar: a, surface Atlantic; b, deep Atlantic; c, shelf Atlantic; d, deep Mediterranean. Salinity and trace-metal data from refs 2 and R. M. Sherrell and E.B. (unpublished). Station locations are centred on horizontal bars. Length of bar is proportional to each end-member contribution. Bars are not drawn to the same scale from one figure to the other. The 8% contour is shown in Fig. 3c for shelf end-member fraction (broken line).

of Gibraltar (Fig. 1). Cd concentrations of open-ocean surface Atlantic waters are usually <10 pM, whereas Cd concentrations of 200 pM are seen in waters overlying the Spanish shelf. These high-Cd waters are found as close as 30 km west of the Strait. Even a small contribution of waters from this area would significantly influence the composition of inflow to the Mediterranean Sea. Similar enrichments have been observed in other coastal regions[6,7].

Differences in the metal–salinity relationships of the two enriched water masses allow one to distinguish them (Fig. 2). Salinity and cadmium concentration gradients within the top 400 m of an open Atlantic profile taken 100 km west of the Strait can be described as a simple mixture of surface Atlantic and deeper (less saline) North Atlantic Central Water (Fig. 2a; data in ref. 2). Cd concentrations in low-salinity Spanish shelf samples follow a different metal–salinity relationship. Some Cd-enriched surface samples were also analysed for Cu, Ni and Zn. Cu and Zn are highly enriched in shelf waters, again showing clear differences between shelf and open-ocean metal–salinity relationships (Fig. 2b and c). Ni enrichment also occurs in shelf waters but is not as dramatic as for the other metals (Fig. 2d). Table 1 gives the composition of end-members representative of the different source areas.

Metal–salinity systematics in shelf samples do not reveal trace-metal enrichment mechanisms because turbulent mixing over the shelf homogenizes these waters and obscures sources or processes leading to the enrichment. Several explanations for these enrichments can be considered. (1) A linear metal–salinity relationship could be due to mixing of metal-enriched river water and open-ocean sea water. A river source of this magnitude is not plausible here because extrapolation of the metal–salinity relationship to zero salinity requires an unrealistically high concentration of metals in the river water. (2) Local fallout of aeolian particles could enrich coastal waters more than open-ocean waters owing to the proximity of a continental aerosol source. But most studies suggest a more gradual decrease in aeolian deposition rates with distance from the coast than we observe for trace-metal enrichments in the Gulf of Cadiz. (3) Diagenesis within shelf sediments may result in diffusion of trace metals into the overlying water[8]. Such a source may be important, but it is difficult to establish the dominance of this mechanism compared with other plausible enrichment processes. (4) A coastal estuarine 'nutrient trap' can increase the residence time of biologically reactive elements such as trace metals over the shelf, thereby increasing their concentration in these waters. The 'source' in this case is simply the inflowing

Table 1 Tracer composition of model end-members and average inflow

Tracer	Surf. Atlantic	Deep Atlantic	Shelf Atlantic	Deep Mediterranean	Model error	Average inflow
Salinity (‰)	36.46	35.70	36.00	38.45	0.05	36.20
Cu (nM)	1.3	1.3	10.0	2.0	0.3	2.8
Ni (nM)	1.8	2.7	3.5	4.2	0.5	2.3
Cd (pM)	20	140	260	60	10	86
Zn (nM)	0.8	1.5	40.00	5.0	0.5	6.8

Following the notation in the text, the weighted least-square solution of end-member fractions for each surface sample is $f = (A^t \cdot W \cdot A)^{-1} \cdot A^t \cdot W \cdot d$ (refs 14 and 15, p.54). W is a diagonal matrix composed of the inverse of estimated model uncertainty for each tracer. Matrix W renders the problem non-dimensional by dividing all tracer values by corresponding model uncertainties. These are also listed above for each tracer. Uncertainty estimates are greater than (salinity) or equal to (trace metals) analytical errors and represent the degree to which the model is required to fit the data for a given tracer. The Kuhn-Tucker theorem provides an iterative solution to this problem as described in ref. 15, pp 126–131. Average inflow composition is based on contributions from surface, deep and shelf Atlantic end-members of 60, 25 and 15% respectively.

open-ocean sea water, from which metals and nutrients accumulate during particulate transfer and remineralization[9]. The circulation regime on the Spanish coast is conducive to such a nutrient trap because of significant freshwater input, whereas the Moroccan coast is not.

Although the evidence cannot distinguish unequivocally between these mechanisms, the sedimentary fluxes and nutrient trap hypotheses are the most plausible explanations for trace-metal enrichments on the Spanish shelf. Whatever the actual shelf enrichment process is, for our purpose the data can be interpreted as the result of mixing of a surface ((A) in Fig. 2) and a deep (B) Atlantic end-member as well as a shelf (D) end-member mixing in various proportions. A salinity of 36.00‰ was chosen for the shelf end-member based on the predominance of this water mass over the shelf west of the Strait. Trace-metal concentrations corresponding to this salinity are included in Table 1.

Four sources of water influence the trace-metal composition of the Alboran Sea inflow plume: (1) Atlantic surface waters, with low metal concentrations, (2) subsurface Atlantic waters; this trace-metal-rich water may be brought to the surface by mixing or upwelling during transport into the Alboran Sea, (3) Spanish continental shelf water, and (4) saline Levantine Intermediate water, which is entrained by mixing and upwelling. Owing to upwelling and clockwise rotation of the Alboran Sea gyre, this deeper Mediterranean water outcrops at the northern edge. Table 1 gives the composition of the deep Mediterranean water mass, which is nearly uniform below 200 m for these tracers[2], along with the three Atlantic end-members defined above. Aeolian particle transport and deposition also may cause surface-water metal enrichments in some environments, but we will demonstrate that Alboran Sea metal distributions can be accounted for without invoking atmospheric sources. Given the rapid circulation of surface waters in the region, conservative mixing (in terms of salinity and trace metal content) is assumed for the Alboran Sea. Residence times of ^{210}Pb in surface waters range from two years in the open ocean[10] to less than a month in the highly productive Gulf of California[11]. The assumption of conservative behaviour for elements that are less particle-reactive than Pb in the Alboran Sea therefore seems justified in view of the vigorous circulation. Based on this hypothesis, trace-metal distributions in the Atlantic inflow east of the Strait, which have been presented elsewhere[2], will be related to the inflow sources.

Assuming conservative mixing of salinity and trace metals, each Alboran Sea surface sample can be described as a linear combination of four distinct end-members. In this expression, the weight of an end-member is the fraction of the total sample contributed by each source. In matrix notation, this relationship can be expressed as $A \cdot f = d$, where A is a model matrix whose four columns contain the tracer composition of each end-member, d is the observed composition of a specific Alboran Sea sample and f is a column vector whose four elements are

the fractions of each contributing source which we want to estimate. The fractions of each end-member are constrained to lie in the range 0 to 1 and sum to unity. The system is over-determined, so analytical errors (and a small degree of non-conservative behaviour) mean that the solution will not match the data perfectly. Figure 3 shows the least-square solutions for f (see Table 1 for details) for each sample. Although each tracer constrains the final solution for all components, the solution for particular components is most sensitive to certain tracers: salinity dominates the estimate for the fraction of deep Mediterranean water, Zn and Cu dominate the estimate for the shelf end-member, and Cd dominates the estimate for the deep Atlantic contribution. Model trace-metal concentrations match data for all five tracers within one 'model error' (defined in Table 1) at each of the 43 surface stations except three, where Cu and Ni residuals are significant. The very good agreement between model fit and observed tracer concentrations indicates that the conservative mixing model is consistent with the data. Even though temporal variations of trace metal relationships over the Atlantic shelf and in the Alboran Sea must still be determined, these results indicate consistency of two data sets collected four years apart during different seasons (June 1982 and April 1986).

Surface circulation features of the Alboran Sea (such as the clockwise rotation of the gyre and injection of Atlantic water through the Strait), are well characterized by satellite thermal imagery and can be compared with the areal distribution of end-members derived above. Surface Atlantic water clearly dominates the upper water column of the Alboran Sea (50–85% of total in Fig. 3a) with the exception of the northern margin of the gyre, where outcropping deep Mediterranean water contributes up to 60% to surface waters (Fig. 3d). This feature can be detected on the basis of salinity alone. Perhaps more interesting is the fact that Cd concentrations in this high-salinity region constrain the solution to include up to 30% of Atlantic deep water (Fig. 3b). A second feature, which is uniquely deduced from trace metal concentrations, is the entrainment of Spanish shelf water in the Atlantic inflow as visualized by the 8% contribution contour of this end-member in Fig. 3c. This result is mainly constrained by Cu and Zn data.

Because the composition of the Atlantic inflow in the Alboran Sea can de described as the result of mixing of three end-members identified in the eastern Atlantic, one can estimate the integrated contribution of each source to the Mediterranean at the time of the observations. Geostrophic calculations show that mass transport through a portion of the transect (from 36°01' N, 5°05' W to 36°09' N, 5°11' W) of the ¿Donde Va? survey[12] is representative of the flux passing through the Strait. In addition, trace-metal and salinity data from a profile centred on this transect (ref. 2 and unpublished results) indicate that the relative composition of the combined Atlantic end-members is constant at a given location even though the total Atlantic contribution decreases with depth relative to that of the Mediterranean component. At each station, a homogenized Atlantic end-member

mixes vertically with Mediterranean water, but the composition of the pre-mixed Atlantic end-member varies from one surface station to the next, as Fig. 3 shows.

Based on these observations and a geostrophic velocity section from ref. 12, a representative composition of the total inflow can be calculated by weighting average metal fluxes of Atlantic origin vertically under each surface station and laterally along the geostrophic section. The resulting average composition of the inflow (see Table 1) is roughly equivalent to that of the deep Mediterranean except for Ni. Keeping in mind that the composition and volume[13] of the inflow probably varies seasonally, it appears that a net source of trace metals within the Mediterranean basin exists for Ni but is less important for Cu, Cd and Zn.

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Evidence for ≥C₃ alkyl nitrates in rural and remote atmospheres

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Interactions of odd-nitrogen compounds with non-methane hydrocarbons and a variety of radical species have been shown to have a potential impact on atmospheric chemistry on local, regional, and even global scales[1-9]. To understand the interactions of atmospheric nitrogen compounds requires an accurate budget of individual reactive nitrogen species. But recent attempts to obtain a mass balance between total reactive nitrogen (NO_y) and individual reactive nitrogen species ($NO + NO_2 + HNO_3 + PAN$ (peroxyacetyl nitrate) + PPN (peroxypropionyl nitrate) + particulate NO_3^-) have not accounted for all NO_y[9,10]. One class of compound proposed to account for some of the NO_y deficit is the alkyl nitrates $(RONO_2)$[5,10-12], although ambient measurements have not been available to test this hypothesis. Here I report measurements of $RONO_2$ made in the North Pacific atmosphere, providing the first direct evidence for existence and transport of ≥C₃ alkyl nitrates in the troposphere. I also observed a variation in alkyl nitrate concentration which suggests these compounds may be used as unique tracers of 'polluted' air masses to remote areas. These observations are significant because relatively long-lived alkyl nitrates can serve as reservoirs of reactive nitrogen in the
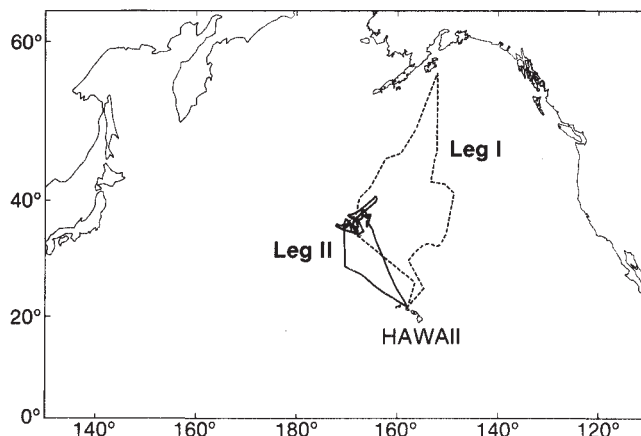

Fig. 1   Cruise track of the RV *Moana Wave* during the SEAREX North Pacific Experiment. Leg I, 28 April to 3 June 1986; leg II, 9 June to 14 July 1986.

remote troposphere, where they can be converted to NO_x, a key catalyst in ozone formation and destruction[3,4].

Alkyl nitrates were measured in air samples collected during a SEAREX (Sea-Air Exchange) cruise in the North Pacific Ocean during April–July 1986 (see Fig. 1). During the cruise two types of samples were taken. Long-term (16–20 h) samples were obtained from a specially constructed air-sampling tower ∼7 m above the deck at the bow of the ship. Typical sample volume for these samples was ∼300 l. Short-term samples were taken from a mast extending several feet in front of the bow. These samples were usually taken during the morning for approximately 30 min. These samples were ∼12 l. All sampling was conducted only with wind coming over the bow of the ship at >5 m.p.h. This excluded possible contamination from ship exhaust. Continuous measurement of condensation nuclei and other chemical data further confirmed the absence of ship contamination during sampling.

Samples were obtained by drawing air at 200–400 ml min⁻¹ through two 5-mg charcoal traps in series. For all analyses reported here there was <5% breakthrough of analytes into the backup trap. After sample collection, the traps were spiked with internal standard and extracted three times with purified benzene. High-resolution capillary gas-chromatographic analysis of the extract was performed using a Varian 3500 GC with an electron-capture detector (ECD). Several major unknown peaks were always observed in the sample extracts during the cruise. Subsequent tests revealed these unknowns as alkyl nitrates.

Identification of the alkyl nitrates was performed on preserved samples in a shore-based laboratory by using gas chromatography–mass spectrometry in the negative-ion chemical ionization (NICI) mode. A mass spectrum of the major unknown compounds from marine samples (Fig. 2) showed that the unknown compound was also present in relatively high concentration in local ambient air; thus most mass spectrometry experiments were done on local air extracts to preserve the few marine samples available. In the local samples not only were there major fragments at m/e 46 and 71, but the m/e 46 fragment was present in a homologous series of compounds following $m/e = 57 + n \times 14$, with $n = 0-5$ (see Fig. 3); the single most abundant compound was at $m/e = 71$. The $m/e = 46$ fragment suggested NO_2, and $\Delta(m/e) = 14$ suggested CH_2, but the negative ion fragment at $m/e = 71$ was a puzzle.

The conclusion that alkyl nitrates could produce the observed NICI mass spectrum was suggested by reports that, in the CI process, alkoxide ions are stabilized by loss of H_2[14]. This phenomenon is widely observed in ion-cyclotron resonance studies of reactions of alkoxide ions with many organic species[15]. NICI-MS of purchased and/or synthesized alkyl nitrates