

MARITIME INFLUENCES ON THE ATMOSPHERIC AEROSOL  
COMPOSITION

R. Van Grieken

Department of Chemistry

University of Antwerp (U.I.A.)

B-2610 Wilrijk, Belgium

15389

Introduction

Until recently chemical oceanographers have paid little attention to the ocean-atmosphere boundary layer. Yet through this interface occur the emission of 85 % of the water vapour that ultimately results in precipitation, the vitally important uptake of oxygen and the absorption of most of the excess carbon dioxide produced by man-made pollution.

Apart from gas exchange, however, there is an important interaction of liquid and solid particulate matter between the ocean and the atmosphere. The importance of these processes for the transfer of pollutants and natural compounds has only recently been appreciated. It has become clear now that material transport from the atmosphere into the ocean plays a considerable role in the global ocean pollution. Some 25 000 tons of DDT annually reach the oceans through the air. Part of the lead present in the North Sea may be derived from combustion of leaded gasoline in the London metropolitan area. Of the ca. 2 000 million tons annual world petroleum production, 90 million tons reach the oceans through the atmosphere due to evaporation during land based operation, while seepage from off-shore oil wells, accidents with tankers and deliberate dumping on sea only account for 3 million tons annually. The existence of long range atmospheric transport by the wind can be illustrated by the abundance of Sahara dust being deposited from the air in regions as far downwind as the Caribbean Sea.

Even less trivial is undoubtedly the reverse process, the transfer of natural compounds and pollutants from the sea into the atmosphere. This paper discusses the mechanism of this transfer process and its potential implications. Scientific studies in this field have hitherto been scarce, incomplete and poorly interpreted. Part of this discussion about particle transport from the sea to the air will thus inevitably be based on speculation rather than on concrete facts.

Mechanism of the ocean-atmosphere particle transfer.

On the average about one gas bubble bursts every ten seconds at every  $\text{cm}^2$  of the oceans. Some of these bubbles are produced by degassing of the surface ocean water during the spring period of warming. Each year, for instance, about 300 l of oxygen leave each square meter of the sea surface in the Gulf of Maine. Most of this gas however crosses the

air-sea interface by diffusion, not as air bubbles. The impact of precipitation, both rain and snow, on the sea surface produces some small air bubbles in the water (2). The major source of bubbles in the sea, however, are the whitecaps or breaking waves that form whenever the wind speed is in excess of  $10 - 15 \text{ km h}^{-1}$  (3). A breaking wave entraps air and produces myriads of bubbles that rise swiftly and then burst at the sea surface. About  $10^8$  air bubbles have been found per  $\text{m}^3$  of sea water a few seconds after a whitecap had formed (1). It has been calculated (3) that on the average 3.5 % of the ocean is covered by whitecaps. Assuming a whitecap lifetime and a bubble residence time in the water of 30 - 60 seconds (1) this process accounts for the breaking at the ocean surface of some  $0.1 \text{ bubbles cm}^{-2} \text{ s}^{-1}$ .

Some spray drops are sent into the atmosphere after being torn off mechanically from wave crests by the wind. However, a far more important source of sea water particles in the air is precisely the breaking at the sea-air interface of air bubbles produced by whitecaps. The mechanism of this process is schematically illustrated in Fig. 1. When the air bubble has risen to the surface the film cap that briefly closes off the air bubble explodes and can emit tiny drops into the air. Most of these so-called film drops are smaller than  $1 \mu\text{m}$ , and their number per bursting bubble depends on the bubble size. Bubbles of less than  $300 \mu\text{m}$  do not produce any film drops, but a  $2 \text{ mm}$  bubble gives rise to some 100 film drops, a  $6 \text{ mm}$  bubble up to about 1000. After the film breaking, the spherical bubble air cavity collapses in a remarkable hydrodynamic process while ejecting a jet of water upwards at high speed. This jet soon becomes unstable, and breaks up in two to five so-called jet drops which separately continue upwards into the air. The size of the jet drops is roughly equal to one-tenth of the size of the bubble that produced them. The energy source that accelerates the upward jet is the surface free energy. Blanchard (3) calculated that the top jet drop from a  $2 \text{ mm}$  bubble is ejected at a speed of  $13 \text{ km h}^{-1}$  and reaches a maximum height of  $18 \text{ cm}$  in the air. A  $70 \mu\text{m}$  bubble, on the other hand, ejects its tiny top jet drop at  $300 \text{ km h}^{-1}$ . This jet drop rises only  $1.7 \text{ mm}$  into the air. However, without the frictional drag of the air it would reach no less than  $335 \text{ m}$ . Fig. 2 represents the ejection heights for subsequent jet drops as a function of the bubble diameter. Although the initial ejection height in the air is generally not impressive, it should be born in mind that both jet drops and film drops can be taken up by the wind and by atmospheric turbulences, shrink quickly by evaporation of the water to a third of their original diameter and remain airborne for long periods of time.

It has been shown (5) that the atmospheric sea salt load above the oceans increases considerably with the wind speed, indicating the importance of breaking waves in the production of air bubbles and sea spray. Also the atmospheric salt load decreases linearly with the altitude (5).

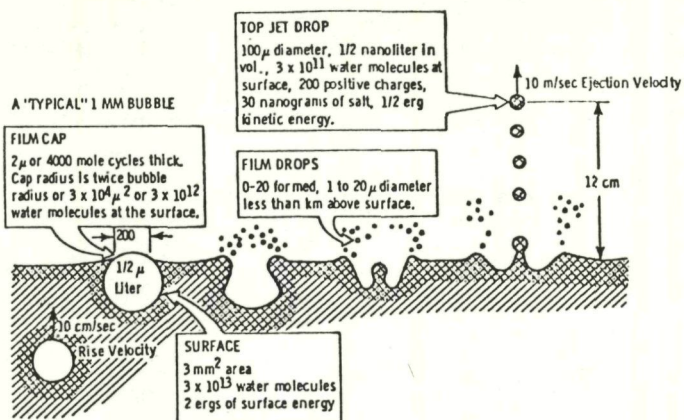


Fig. 1 : Diagrammatic representation of bubble breaking mechanism (from Mac Intyre, Ph.D. Thesis, M.I.T., Cambridge, Mass., 1965, with permission).

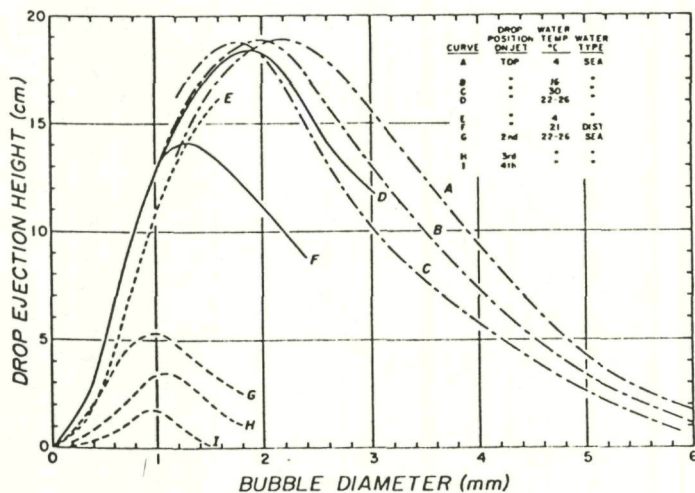


Fig. 2 : Jet drop ejection height as a function of bubble diameter (from Blanchard, ref. (3), with permission).

Table I compares the contribution of the sea as an aerosol source to those of other natural and anthropogenic sources. It appears that 40 % of the global atmospheric aerosol originates from bubble breaking processes in the oceans. Since film drops are formed from the top film of the ocean, their composition will bear little relation to the bulk sea water composition and will be similar to that of the air-water boundary layer.

Table I : Sources of atmospheric aerosols (from Robinson and Robbins, Report SRI 8507, Stanford Research Institute, 1971).

Source	Source strength (in $10^{12} \text{ g yr}^{-1}$ ).	
	Natural	Man-made
<u>Direct particle production</u>		
Sea spray	1000	
Soil dust	200	
Volcanoes	4	
Forest fires	3	
Meteorites	0.1	
Fly-ash from coal		36
Agriculture		10
Steel industry		9
Wood combustion		8
Cement industry		7
Solid waste combustion		4
Petroleum combustion		2
Other activities		16
Subtotals :	1207	92
<u>Gas-particle conversion</u>		
Sulphate from $\text{SO}_2$		147
Nitrate from $\text{NO}_x$	432	30
Ammonium from $\text{NH}_3$	269	
Sulphate from $\text{H}_2\text{S}$	204	
Organic aerosols from terpenes, hydrocarbons,...	200	27
Subtotals :	1105	204
Totals :	2312	296

The source of material for the jet drops, on the other hand, is the thin wall of the bubble just before it collapses. High speed photographs of solutions containing surface active dyes have shown that the bubble wall material collides at the bottom of the bubble cavity from where it rises as a jet. As Fig. 3 illustrates, subsequent material slices as thin as a fraction of a micrometer are skimmed off from the bubble wall to give rise to the subsequent jet drops. Bubbles act like a microtome in this respect, and it has been suggested (6) that the average thickness of ocean surface ejected into the atmosphere by a bubble as jet drops is roughly 0.05 % of the bubble diameter. Clearly, the jet drop composition will be similar to that of the water-air interface that constitutes the bubble wall.

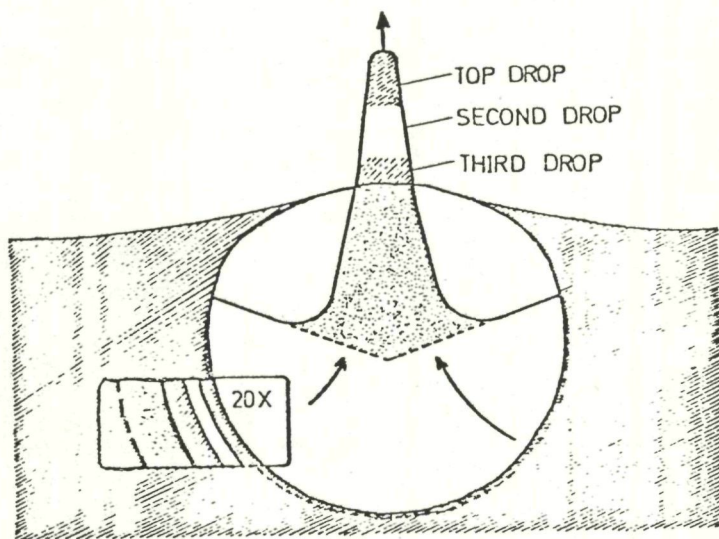


Fig. 3 : Source of drop material in a breaking bubble is the thin wall of the bubble just before collapse.

#### Chemical composition of sea surface layer and air bubble wall.

Bulk sea water contains only little organic material, about  $1 \text{ mg l}^{-1}$ . Of this, phytoplankton, zooplankton and fish constitute less than 2 %. The non-living organic material makes up for 1 % in the particulate form and some 97 % in the dissolved form. The dissolved organic material is mainly derived from living organisms by diffusion of organic molecules during normal growth and from dead organisms by decay. The bulk of these dissolved organics is composed of proteins and protein-derived metabolites (7).

The slicks commonly observed on the sea surface are composed of organic material, highly concentrated at the water-air interface because of the surface-active properties of some organic compounds. Baier et al. (8) believe that the primary compounds are glyco-proteins, which are essentially hydrophilic molecules but concentrate at the interphase because of some hydrophobic side chains. Organic carbon, nitrogen and phosphorus are definitely enriched in this surface layer (9), as are bacteria, dinoflagellates and other plankton (10). Enrichments of DDT of  $10^5$  relative to sub-surface water have been reported (11), and enrichments of heavy metals up to  $10^4$  (12). The latter fact is probably linked to a chelation of transition metal ions with naturally occurring organic complexing agents with surface-active properties, or to Gibbs adsorption. Mac Intyre (13) has given a thorough review of the possible fractionation mechanisms.

Most of the material carried into the air by film drops originates from this surface layer. The jet drops, however, will mainly include the material adsorbed on the surface of the bubble. It is well known that dissolved and particulate surface active organic molecules diffuse towards, and adhere onto the surface of the bubble as it rises through the water. This process is called scavenging, and it is applied e.g. in froth flotation. The only references so far to scavenging with respect to sea-to-air transfer of material report an increased enrichment of tracers (14) and of bacteria (15) in the jet drops, as a function of the rise distance of the bubbles through the water due to an increased material adsorption along the bubble rise path. The jet drop ejection heights decrease as can be expected when the surface free energy is reduced by increased surface active compound adsorption on the rising bubbles (2). Therefore it is certain that adsorption of material during the bubble rise time plays an important role in ocean-atmosphere interaction of particulate matter. The compounds enriched at the bubble wall should be similar to those concentrated at the sea surface.

#### Implications for the atmospheric aerosol.

A first indication for enrichment procedures taking place during the formation of maritime aerosols can be found in the observation that near a beach with surf glasses get greasy rather than salty. Analysis of sea spray has shown organic material contents amounting to 20 to 50 % of the salt content (16). This represents an organic material enrichment of 7000 to 17 000 times, with respect to bulk sea water.

The enrichments during the maritime aerosol production process are also clearly reflected in the composition of rain water, which is normally "exotic" with respect to organic content, halogen ratios (2) and major ions (6).

Organic material enrichment in maritime aerosols seems able to provide sufficient food to high-altitude snow to support invertebrate life in the "aeolian" zone above the vegetation line, and delivers economically significant amounts of plant nutrients to coastal areas (6).

Tiny organisms like the neuston, that lives in the uppermost layer of the ocean, are expected to be concentrated in sea spray. Woodcock (17) found, indeed, that in periods of "red tide blooms" in the Gulf of Mexico the efficient transfer into the air of the toxins from the dinoflagellate *Gymnodinium Breve* was responsible for throat irritations of the people along the shore.

A large fraction of the organic material now afloat on the Baltic, Mediterranean and North Sea, consists of petroleum products. A possible consequence - often overlooked hitherto - is that these petroleum derivatives might drastically change the physico-chemical properties of the ocean surface layer, hence influence the normal bubble breaking mechanism, and also that they could be incorporated to a certain extent in the aerosols produced from the sea, and influence the hygroscopicity of the sea salt particles. Since sea-salt aerosols form most important condensation nuclei, petroleum could influence the formation of rain by the combined effect of smaller particle size and of different latent heat and surface characteristics of the cloud drops. It seems that already, due to local petroleum pollution, the maritime aerosols at some locations South of Genoa, Italy, contain so much petroleum that thousands of pine trees along the shore have died, covered with a suffocating petroleum layer brought along drop by drop through the atmosphere (18). Here we find an impressive example of how bursting bubbles can create an air pollution problem out of what initially was one of water pollution.

Blanchard and Syzdek (19) (20) have found that the bacteria *Serratia Marcescens* is concentrated  $10^4$  times in jet drops relative to the bulk water from which these originate. It has recently been postulated (21) that the geographic distribution of skin sensitivity to *Mycobacterium Intracellulare* antigens may be explained by a marine origin followed by transport to the land of droplets containing the mycobacterium. One can wonder whether transmission of pathogenic bacteria through the air from biologically polluted seas cannot be a hazard to the people downwind. Perhaps one should take into account the prevalent wind direction and frequency of breaking waves in selecting the sites for sewage pipeline outlets and for large scale waste dumping into the sea. Finally treatment of sewage and waste water often involves bubbling of air through the liquid, and again, perhaps we ought to worry about the possibility of enrichment into the aerosols that are generated in this aeration process.

Enrichment of DDT and trace elements in aerosols from breaking bubbles seems quite probable, in view of their important enrichment in the ocean surface layer (11) (12). Hitherto nobody has done the crucial laboratory experiment to prove this, however. It is well known that in aerosols sampled both over the continent and the ocean, even as far from industrial areas as Antarctica (22), certain metals are found in much higher relative concentrations than expected from sea salt or average soil dispersal, e.g. Se, Sb, Pb, Cu, Zn. Several interpretations have been suggested for this phenomenon, as selective evaporation from rocks or preferential emanations from plant material. Up to now however the fractionation and enrichment of chelated ions during the bubble breaking process cannot yet be ruled out completely as an alternative interpretation.

In earlier laboratory experiments on ion fractionation, Mac Intyre and Winchester (23) have observed enrichments of phosphate ions by a factor of thousand for certain particle size ranges, if one takes  $\text{Na}^+$  as a reference and assumes that  $\text{Na}^+$  does not suffer any fractionation due to its abundance and ionic character.

Later on we have studied the fractionation of some radioactive nuclides (14) (24). Radioactive tracers ( $^{65}\text{Zn}$ ,  $^{75}\text{Se}$ ,  $^{137}\text{Cs}$ ,  $^{152}\text{Eu}$  and  $^{22}\text{Na}$ ) were added to a beaker with natural sea water. Then an air stream was bubbled through the solution and the resulting aerosol was drawn through a cascade impactor, a simple aerodynamic device that collects aerosol particles in different stages according to their size. Typically 30 ml of sea water was used, collected a few hours before on a Gulf of Mexico beach, and air bubbles of 0.1 to 3 mm diameter rising 1 or 10 cm through the solution. The impaction surfaces with the aerosol deposits were measured by gamma spectrometry. As a measure for the enrichment of e.g.  $^{65}\text{Zn}$ , one can define a fractionation factor F :

$$F = \frac{(\text{Activity } ^{65}\text{Zn} / \text{Activity } ^{22}\text{Na}) \text{ in aerosol}}{(\text{Activity } ^{65}\text{Zn} / \text{Activity } ^{22}\text{Na}) \text{ in sea water}}$$

We found that the observed enrichments varied systematically with the particles size, were proportional to the rise distance of the bubbles through the solution, and depended on the air bubble size, on the equilibration time of the tracers in the sea water and on the natural substances in the seawater which are influenced by the tide and previous abundant rainfall. For  $^{65}\text{Zn}$ , fractionation factors up to 50 were found, and one can expect more important effects in natural circumstances involving rise distances of several meters in breaking waves. In considerations on the safety and the environmental implications of off-shore nuclear power plants, no attention was paid hitherto to the possibility of efficient transfer of radioactive waste products from the ocean to the atmosphere. Yet in this way in case of an accidental spill or routine dumping the radioactivity might reach the people along the coast much faster than expected from sea currents and diffusion phenomena. It remains an open question whether for average nuclear reactor waste, the transfer into the atmosphere would have more than a merely academic importance. Yet the possible implications involved seem to warrant a thorough study.

### Conclusion

The few cited examples of ocean-atmosphere interactions demonstrate the importance of the ocean surface layer for the life and well being on earth, mainly because the ocean is decisive for most of the global atmospheric aerosol load. In this way water and air pollution are no separate problems but show a distinct link in some cases. Perhaps in no other region of the environment do subtle physico-chemical and hydrodynamic properties influence global geophysical and geochemical phenomena so profoundly as in the transfer processes between air and water. In the absence of exact scientific data, part of the cited possible con-

sequences of air-sea interactions are speculative, and perhaps not globally important. Yet it would seem unwise at present therefore not to consider them.

### References

1. Blanchard, D.C. and A.H. Woodcock : "Bubble formation and modification in the sea and its meteorological significance", *Tellus* 9, (1957), 145-158.
2. Blanchard, D.C. : "Bubble scavenging and the water-to-air transfer of organic material in the sea", in "Applied Chemistry at Protein Interfaces", *Advances in Chemistry Series*, Number 145; American Chemical Society, (1975), p. 360-387.
3. Blanchard, D.C. : "The electrification of the atmosphere by particles from bubbles in the sea", *Prog. Oceanog.*, 1 (1963), 71-202.
4. Woodcock, A.H., C.F. Kientzler, A.B. Arons and D.C. Blanchard : "Giant condensation nuclei from bursting bubbles", *Nature* 172, (1953), 1144.
5. Woodcock, A.H. : "Salt nuclei in marine air as a function of altitude and wind force", *J. Meteorol.*, 10 (1953), 362-371.
6. Mac Intyre F. : "The top millimeter of the ocean", *Scientific American*, 230 (1974), 62-77.
7. Hood, D.W. (editor) : "Organic matter in natural waters", University of Alaska, (1970), 625 pg.
8. Baier, R.E., D.W. Goupel, S. Perlmutter and R. King : "Dominant chemical composition of sea surface films, natural slicks and foams", *J. Rech. Atmosph. VIII* (1974), 571-600.
9. Williams, P.M. : "Sea surface chemistry : organic carbon and organic and inorganic nitrogen and phosphorus in surface films and subsurface waters", *Deep Sea Res.*, 14 (1967), 791-799.
10. Harvey, G.W. : "Microlayer collection from the sea surface : a new method and initial results", *Limn. and Oceanog.* 11 (1966), 608-613.
11. Seba, D.B. and E.F. Coreoran : "Surface slicks as concentrators of pesticides in the marine environment", *Pesticides Monit. J.* 3 (1969), 190-193.
12. Duce, R.A., J.G. Quinn, C.E. Olney, S.R. Piotrowicz, B.J. Ray and T.L. Wade : "Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island", *Science*, 176 (1972), 161-163.
13. Mac Intyre, F. : "Chemical fractionation and sea surface microlayer processes", in *The Sea*, Vol. 5, Marine Chemistry, E.D. Goldberg, ed., John Wiley & Sons, Inc. New York, pg. 245-299.
14. Van Grieken, R.E., T.B. Johansson and J.W. Winchester : "Trace metal fractionation effects between sea water and aerosols from bubble bursting", *J. Rech. Atmosph. VIII* (1974), 611-621.
15. Blanchard, D.C. and L.D. Syzdek : "Concentration of bacteria in jet drops from bursting bubbles", *J. Geophys. Res.* 77, (1972), 5087-5099.
16. Blanchard, D.C. : "Sea-to-air transport of surface active material", *Science* 146 (1964), 396-397.
17. Woodcock, A.H. : "Note concerning human respiratory irritation associated with high concentration of plankton and mass mortality of marine organisms", *J. Marine Res.* 7 (1948), 56-61.

18. Blanchard, D.C. : "The borderland of burning bubbles", Saturday Review, January 1, 1972, pg. 60-63.
19. Blanchard, D.C. and L.D. Syzdek : "Mechanism for the water-to-air transfer and concentration of bacteria", Science 170 (1970), 626-628.
20. Blanchard, D.C. and L.D. Syzdek : "Concentration of bacteria in jet drops from bursting bubbles", J. Geophys. Res., 77 (1972), 5087-5099.
21. Gruft, H., J. Katz and D.C. Blanchard : "Postulated source of Mycobacterium Intracellulare (Battey) infection", Am. J. of Epidemiology 102 (1975), 311-318.
22. Duce, R.A., G.L. Hofmann and W.H. Zoller : "Atmospheric trace metals at remote northern and southern hemisphere sites : pollution or natural?", Science 187 (1975), 59-61.
23. Mac Intyre, F. and J.W. Winchester : "Phosphate enrichment in drops from breaking bubbles", J. Phys. Chem., 73 (1969), 2163-2169.
24. Van Grieken, R.E., T.B. Johansson, J.W. Winchester, D.L. Meinert and W.W. Berg, Jr. : "Laboratory tracer experiments on fractionation during bubble bursting", Florida State University, Department of Oceanography, Technical Report 8-74 (1974).